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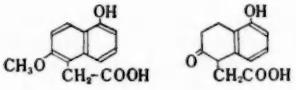
*Abnormal Reduction of 2-Methoxy-5-hydroxy-1-naphthylacetic Acid**

By Takeshi MATSUMOTO and Akira SUZUKI

(Received February 20, 1959)

In the previous paper[1] the synthesis of 2-methoxy-5-hydroxy-1-naphthylacetic acid (I) was described. The present work was undertaken in an attempt to prepare 1,2,-3,4-tetrahydro-2-oxo-5-hydroxy-1-naphthylacetic acid (II), a potential intermediate for building up the diterpenoid alkaloid framework, by reduction I.



(I) (II)

It is well known that the reduction of a variety of 2-methoxynaphthalene derivatives by alkali metal in alcohol[2] or in alcohol-liquid ammonia[3] yields the corresponding 2-oxotetralins. At first sight, therefore, it seemed easy to prepare tetrahydro-2-oxo-5-hydroxy-1-naphthylacetic acid (II). However, attempted reduction along this line led to unusual results. Depending upon the procedure employed, tetrahydro-5-hydroxy-1-naphthylacetic acid (III) or a mixture of compound III and tetrahydro-2-oxo-4,5-dihydroxy-1-naphthylacetic acid (IV) has been obtained.

At first, the reduction was effected by employing a large excess of sodium (ca. 0.03 mol. per 0.001 mol. of I) in butanol. Product A, which was obtained in good yield, unexpectedly did not react with dinitrophenylhydrazine. The elemental composition corresponded to $C_{12}H_{14}O_3$ rather than to that of the expected product II, $C_{12}H_{12}O_4$. The tests for a methoxyl group (Zeisel) and for a secondary alcohol group (Nessler) were both negative. The infrared spectrum in nujol mull possessed a single sharp band at 1700 cm^{-1} (carboxyl group) and a broad absorption band at 3200~3400 cm^{-1}. Of three oxygen atoms, two have thus been shown to be present in a carboxyl group, and one probably as a hydroxyl group. The presence of a hydroxyl group was confirmed by the formation of monoacetate, $C_{14}H_{16}O_4$. The ultraviolet spectrum (Fig 2. curve b) of product A could be superimposed upon that of 1,2,3,4-tetrahydro-5-naphthol (curve c). These results clearly indicate that product A should be expressed by formula III. So far as the authors are aware, the ready conversion of methoxynaphthalenes to desoxygenated tetralins has not hitherto been reported[4]. The formation of the abnormal reduction product must be attributed, at least in part, to the presence

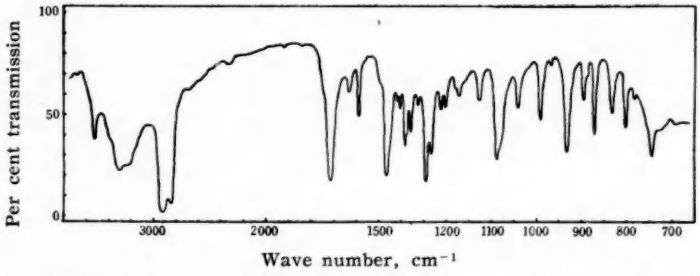


Fig. 1. Infrared spectrum of 1,2,3,4-tetrahydro-2-oxo-4,5-dihydroxy-1-naphthylacetic acid (IV).

* Approaches to the Synthesis of Diterpenoid Alkaloid Models. II.

1) T. Matsumoto and A. Suzuki, This Bulletin, in preparation.

2) For example, U. W. Cornforth and R. Robinson, *J. Chem. Soc.*, **1949**, 1861.

3) A. J. Birch and H. Smith, *Quart. Revs.*, **12**, 17 (1958).

4) A. L. Wilds et al., *J. Am. Chem. Soc.*, **95**, 5360 (1953), have obtained Δ^{9-10}-octahydronaphthalene as a by-product (10~16%) from 5,6,7,8-tetrahydro-1-methoxynaphthalene by reduction with lithium in alcohol-liquid ammonia.

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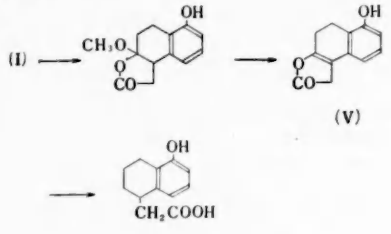
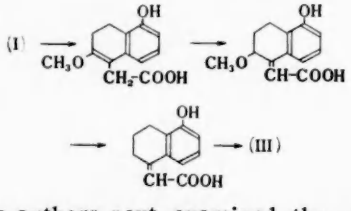
of a carboxyl group, since 1-methyl-2-methoxy-5-hydroxynaphthalene is reported to give smoothly tetrahydro-1-methyl-2-oxo-5-hydroxynaphthalene[5]. On the other hand, Jacobs and Scott[6] have observed that $\beta\gamma$-unsaturated-γ-lactones are susceptible to catalytic hydrogenolysis to form saturated acids, whereas $\alpha\beta$-isomers give saturated lactones on catalytic hydrogenation. The authors are not aware of any example of reductive cleavage of $\beta\gamma$-unsaturated-γ-lactone by means of sodium and alcohol. Nevertheless, it seemed likely at that time that the abnormal reduction proceeds under the participation of the carboxyl group through a $\beta\gamma$-unsaturated-γ-lactone such as V as shown below:



According to this assumption, treatment of methyl ester of I, rather than I itself, under the same conditions was expected to afford methyl ester of the desired tetralone (II). However, reduction of the methyl ester of I with subsequent hydrolysis gave again the tetralin derivative III as a main product. The above assumption therefore became improbable; the tetralin derivative III might be formed through a process which involves reductive elimination of the allylic methoxyl group as outlined below, but further evidence is required to elucidate the pathway.



The authors next examined the reduction employing sodium and boiling ethanol as well as sodium and ethanol-liquid ammonia (Birch's conditions). In both cases most of the starting material was recovered, in the former case, probably because of the low reaction temperature and in the latter case, probably owing to the extreme low solubility[7] of the naphthylacetic acid in liquid ammonia. Attempts to reduce I by means of lithium in ethanol-liquid ammonia-dimethoxyethane (Wild's procedure) led to the formation of tetrahydro-5-hydroxy-1-naphthylacetic acid (III) in good yield, even when only 4.7 g. atoms per mol. of lithium was used[8].

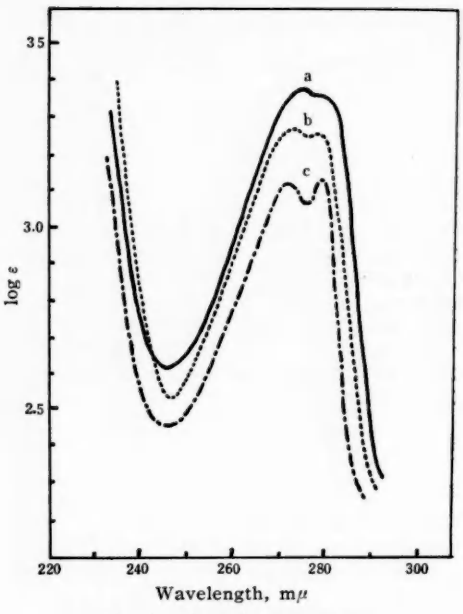


Fig. 2. Ultraviolet spectra.
a (——): 1,2,3,4-Tetrahydro-2-oxo-4,5-dihydroxy-1-naphthylacetic acid (IV) in methanol.
b (------): 1,2,3,4-Tetrahydro-5-hydroxy-1-naphthylacetic acid (III) in methanol.
c (-----): 1,2,3,4-Tetrahydro-5-naphthol in cyclohexane.

Since all efforts to prepare III were thus unsuccessful, attention was turned again to the first method. The reduction was carried out at this time employing a smaller amount than before (8 atoms per mol.) of sodium. From the resulting reaction mixture, an appreciable amount of a carbonyl compound B, m. p. 121.5~123°C was isolated through its triethylamine salt, together with tetrahydro-5-hydroxy-1-naphthylacetic acid (III) and the

5) Ref. 2.
6) W. A. Jacobs and A. B. Scott, *J. Biol. Chem.*, 87, 601 (1930).
7) For similar examples, see Ref. 3.
8) In this case a portion of the starting material was recovered; see *Experimental Section* below.

unchanged starting material I. Elemental analysis of the carbonyl compound B indicated the formula $C_{12}H_{14}O_6$. The infrared spectrum (Fig. 1) of this compound exhibited absorption bands at 3550 and 1635 cm^{-1} (solvated water), which disappear in a sample dried at 80°C in high vacuum, a broad band extending from 3400 to 3200 cm^{-1} (associated OH) and a single broad band at the carbonyl region (probably superimposed carboxyl and carbonyl bands). The ultraviolet spectrum (Fig. 2, curve a) of the hydrated substance showed almost the same shape as those of 1, 2, 3, 4-tetrahydro-5-naphthol (curve c) and 1, 2, 3, 4-tetrahydro-5-hydroxy-1-naphthylacetic acid (III) (curve b).

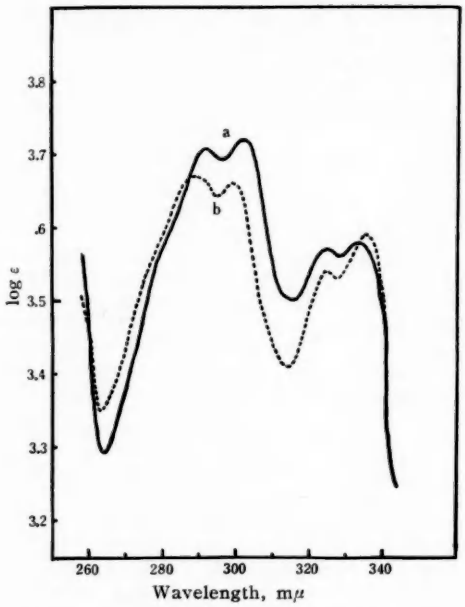


Fig. 3. Ultraviolet spectra in methanol.
a (——): 2-Methoxy-5-hydroxyl-1-naphthylacetic acid (I).
b (------): Methyl 2, 5-dihydroxy-1-naphthylacetate (VI).

At this stage the authors supposed that they had the desired product II ($C_{12}H_{12}O_4$) with two moles of water of crystallization at hand, although analytical values for carbon and hydrogen agreed better with $C_{12}H_{14}O_6$. Drying at 80°C in high vacuum was accompanied by decomposition of product B and an analytically pure anhydrous sample could not be obtained. To confirm the above hypothesis, preparation of the methyl ester was then attempted. Contrary to the expectation, treatment with methanolic hydrogen chloride led to two naphthalene derivatives. Presence of the 1-naphthol chromophore in both the products was clearly demonstrated by their ultraviolet spectra. One of the products, $C_{14}H_{14}O_4$, m. p. 155.5~156.5°C, ν_{max}^{nujol} 3420(OH) and 1735 cm^{-1} (ester) exhibited positive Zeisel test and was readily identified with methyl 2-methoxy-5-hydroxy-1-naphthylacetate (VII)[1], which was obtained separately by esterification of I. The other product, $C_{13}H_{12}O_4$, m. p. 183~184°C, ν_{max}^{nujol} 3480 (OH) and 1740 cm^{-1} (ester) was formulated as methyl 2, 5-dihydroxy-1-naphthylacetate (VI) on the basis of analytical and spectral data (ultraviolet spectrum; Fig. 3, curve b). Formation of these naphthalene derivatives suggests strongly that product B, $C_{12}H_{14}O_6$, is actually a monohydrate of tetrahydro-2-oxo-5-hydroxy-1-naphthylacetic acid with an additional hydroxyl group on the aliphatic portion. Presence of two hydroxyl groups was proved by the formation of a diacetate, $C_{16}H_{14}O_6$. The infrared spectrum (Fig. 4) of the diacetate showed complete absence of a hydroxyl function and presence of the following groups: $\beta\gamma$-unsaturated-γ-lactone (1795 cm^{-1}), phenyl acetate (1765 cm^{-1}) and saturated ester (1745 cm^{-1}). Therefore, a structural formula like VIII is concluded for this

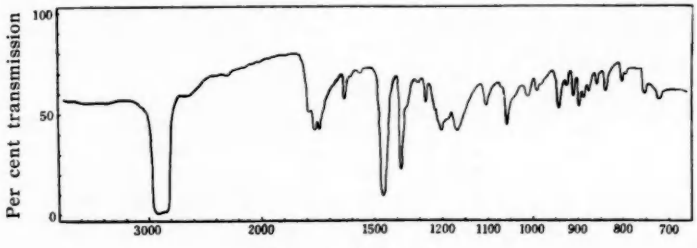
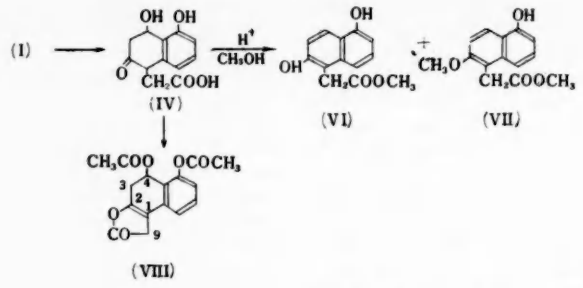


Fig. 4. Infrared spectrum of VIII.



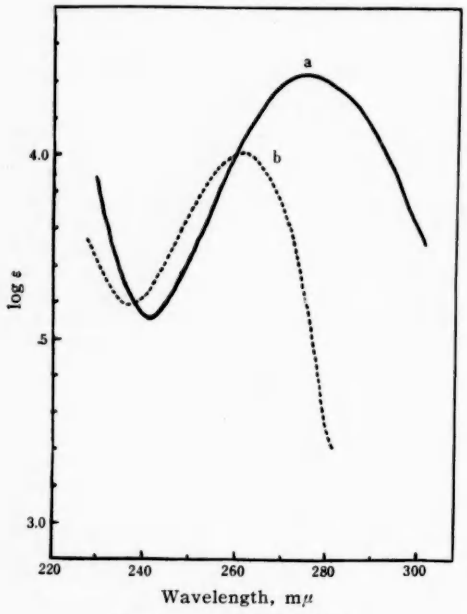
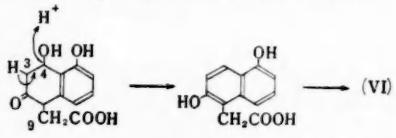


Fig. 5. Ultraviolet spectra.
a (——): VIII in methanol.
b (------): 1,2-Dihydronaphthalene in *n*-hexane.

compound*. The ultraviolet spectrum[9] (Fig. 5, curve a) seems also to agree with this formula. There is a bathochromic shift and an increase in absorption intensity as compared with the spectrum (curve b) of the parent hydrocarbon, 1,2-dihydronaphthalene; these changes can be reasonably ascribed to the presence of an enolic and of a phenolic acyloxy group on the conjugated system.

From formula VIII thus assigned to the diacetate, it follows that two hydroxyl groups (except one hydroxyl group of water of crystallization) are present in product B, and moreover, the hydroxyl group does not occupy the 1-position.

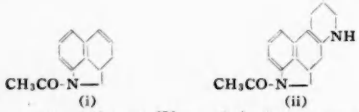
Concerning the position of the aliphatic hydroxyl group in compound B, there remain possibilities of its presence at C_3, C_4 and C_9 positions, of which the C_4 position is the most likely one, since the formation of the naphthalene derivatives[10] is readily explained by a β-elimination reaction:



However, the possibilities of C_3 and C_9 positions can not be conclusively excluded at this stage, since substituents at these positions, being placed respectively at $\alpha\beta$-position to the phenyl and carbonyl groups, are expected to be also susceptible to undergoing an elimination reaction. In the case of C_9 position, subsequent rearrangement of the resultant unsaturated compound would lead to the naphthalene derivatives. The presence of the hydroxyl group at the C_4 position, however, has been demonstrated by the following evidence: product B does not reduce triphenyltetrazolium chloride and hence does not contain an α-ketol system, and moreover, the fact that p*K*a value (6.20) of the product is very close to that (6.12)

* At this stage the position of the alicyclic acetoxyl group is uncertain.

9) Compound i has been reported to possess bands at 241, (ε 22500), 254 (ε 23000), 307 (ε 1600) and 316 (ε 1300) mμ; absorption bands at 252 (ε 2060) and 328 (ε 1500) mμ are recorded for compound ii. E. C. Kornfeld, E. J. Kornfeld, G. B. Kline, M. T. Mann, D. E. Morrison, R. G. Jones and R. B. Woodward, *J. Am. Chem. Soc.*, **78**, 3087 (1956).



Low ε max value at 252 mμ of the latter compound is quite unusual.

10) 2-Naphthols are readily methylated by methanol in the presence of acidic catalysts; W. A. Davis, *J. Chem. Soc.*, **77**, 33 (1900).

of the tetrahydro-5-hydroxy-1-naphthylacetic acid (III), clearly indicates that the hydroxyl group is not located at the α-position (C_9) relative to carboxylic function. Although the structure of product B has thus been shown to be IV, the mechanism of conversion I→IV is quite obscure. No example of this kind of reaction seems ever to have been recorded. Although it is out of the scope of the authors' immediate purpose to study in detail the reaction process, it may be noted that the effective reagent which causes the conversion seems not to be sodium butoxide, but to be sodium itself; IV could not be obtained by a mere boiling of I in butanolic sodium butoxide solution.

Experimental[11]

Reduction of 2-Methoxy-5-hydroxy-1-naphthylacetic Acid (I) with Sodium and *n*-Butanol.—A solution of I (230 mg.; 0.001 mol.) in butanol (7 cc.) was boiled under reflux in an oil-bath at 120~130°C with stirring, sodium (730 mg.; 0.032 g. atom) was added in small pieces during 15 min. A further quantity of butanol (3 cc.) was then added to dissolve precipitated sodium butoxide. When the sodium had completely dissolved, the mixture was poured into an equal volume of water. The alkaline aqueous layer was separated, extracted twice with ether, acidified with concentrated hydrochloric acid and allowed to stand overnight. The crude reduction product, which separated out, was collected by filtration. When the filtrate was extracted three times with ether and the ether was evaporated, an additional amount of the above product was obtained. Total yield, 130 mg. (63%). After recrystallization from water, product A (tetrahydro-5-hydroxy-1-naphthylacetic acid) had m. p. 144~145°C and exhibited ν_{max}^{nujol} 3200~3400 (OH) and 1700 cm^{-1} (CO_2H). Ultraviolet absorption bands at 272 (log ε 3.27) and 278 mμ (log ε 3.26).

Anal. Found: C, 69.79; H, 6.98. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%.

1, 2, 3, 4-Tetrahydro-5-acetoxy-1-naphthylacetic Acid.—The above acid (III) (100 mg.) was dissolved in absolute pyridine (1.5 ml.). Pure acetic anhydride (0.5 ml.) was added with shaking and the reaction mixture was set aside overnight. The most of pyridine and excess of acetic anhydride was then evaporated. To the residue was added 2 N hydrochloric acid and the mixture was extracted three times with ethyl acetate. The extract was washed twice with water, dried and evaporated. The solid residue on being crystallized from ligroin afforded 100 mg. (83.5%) of the acetoxy acid. Recrystallization from ligroin gave an analytical sample as colorless needles, m. p. 125~126.5°C, ν_{max}^{nujol} 1750 (phenylacetate) and 1700 cm^{-1} (CO_2H).

Anal. Found: C, 67.74; H, 6.60. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

1, 2, 3, 4-Tetrahydro-2-oxo-4, 5-dihydroxy-1-naphthylacetic Acid (IV).—To a boiling solution of I (1.84 g.; 0.008 mol.) in 40 cc. of butanol, sodium (1.47 g.; 0.064 g. atom) was added rapidly in small pieces during 10 min. with stirring. After the sodium had completely dissolved, the mixture was treated with 40 cc. of water, and the two layers were separated. After the aqueous layer had been washed twice with ether, 8 cc. of concentrated hydrochloric acid was added under ice cooling and the solution was warmed in a water bath at 70~80°C for 30 min. When the mixture had cooled, an oily substance was separated out; the aqueous layer was then extracted three times with ethyl acetate. The oil and the ethyl acetate extract were combined and the whole was washed twice with water, dried with sodium sulfate, and evaporated to dryness. The oily residue (1.82 g.) was then dissolved in 50 cc. of ethyl acetate; to this solution an excess of triethylamine was added in small portions and the solution was allowed to stand for 5 days. At the end of this period, a considerable amount of triethylamine salt and viscous gum precipitated on the bottom of the flask. The solvent was removed by decantation and the viscous gum was removed by washing the residue quickly with a small amount of cold absolute ethanol. The crystalline triethylamine salt thus obtained melted at 152°C with decomposition.

The salt was then dissolved in 5 cc. of water; the solution was acidified with 6 N hydrochloric acid and extracted with ethyl acetate; the extract was washed with water, dried and evaporated. On being triturated with ether, the residue crystallized to furnish crude tetrahydro-2-oxo-4,5-dihydroxy-1-naphthylacetic acid (IV), which was recrystallized from water as colorless solvated prisms (0.3 g.; 15%), m. p. 121.5~123°C. Ultraviolet absorption band at 274 mμ (log ε 3.38).

Anal. Found: C, 56.92; H, 5.75. Calcd. for $C_{12}H_{12}O_5 \cdot H_2O$: C, 56.69; H, 5.55%.

The viscous part, which was separated from the triethylamine salt of IV, on being acidified with hydrochloric acid afforded a mixture of the starting material and III, which was separated by virtue of higher solubility of the latter compound in water.

Reduction of I by Nelson-Wild's Method.—Sample of compound I (920 mg.; 0.004 mol.) was placed in a three-necked flask equipped with stirrer, dropping funnel and drying tube (soda-lime). To the vessel was added enough anhydrous dimethoxyethane (20 ml.) to dissolve I. The flask was cooled to −40~−50°C. Liquid ammonia (45 ml.) was added to the solution and then lithium (0.5 g.; 0.072 g. atom) in small pieces during 2 min. After stirring for 10 min. absolute

11) All melting points are uncorrected. Infrared spectra were taken on a Koken model DS-301 infrared spectrophotometer with sodium chloride optics. Ultraviolet spectra were measured by means of a Beckman model DK-2 spectrophotometer. The authors are indebted to Mr. O. Yonemitsu of the Pharmaceutical Institute of Hokkaido University for infrared spectra data and to Miss Noriko Fujino for microanalyses.

ethanol was added dropwise for a period of 15 min. When the blue color of the solution had disappeared, ammonia was expelled, the residue was then treated with cold water and acidified with 6 N hydrochloric acid. The acidic aqueous solution was extracted three times with ethyl acetate. After the combined extracts had been washed with saturated sodium chloride solution and dried over sodium sulfate, the solvent was evaporated and the residue was crystallized from water. A yield of 500 mg. (61%) of 1, 2, 3, 4-tetrahydro-5-hydroxy-1-naphthylacetic acid (III) was obtained. Recrystallization from water gave a pure material of m. p. 144~145°C as colorless needles. No depression at the melting point was observed on admixture with the product obtained by the use of sodium and butanol.

When reduction had been effected employing 0.92 g. (0.004 mol.) of compound I, 20 cc. of dimethoxyethane, 50 cc. of ammonia, 0.13 g. (0.0188 mol.) of lithium and 1.2 cc. of ethanol, there were obtained 310 mg. of III and 560 mg. of I. Presence of a small amount of carbonyl compound in the crude reaction product was indicated by the dinitrophenylhydrazine test, but the compound could not be isolated.

Aromatization of Product B.—Sample of product B (210 mg.) was suspended in 5% methanolic hydrogen chloride (10 cc.). The reaction mixture was refluxed on a steam bath for a period of 2 hr. After it had cooled, the solution was evaporated to dryness in vacuo. To the viscous residue were added water and ethyl acetate; the aqueous layer was separated and was re-extracted with ethyl acetate. The combined extracts were washed successively with water, 5% sodium bicarbonate and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removal of the solvent, 192 mg. of a solid product was obtained. Crystallization of the product from benzene gave 50 mg. of methyl 2,5-dihydroxy-1-naphthylacetate (VI) with a melting point 180~183°C, which raised to 183~184°C (decomp.) on recrystallization from benzene. Ultraviolet absorption bands at 288 ($\log \varepsilon$ 3.67), 299 ($\log \varepsilon$ 3.66), 324 ($\log \varepsilon$ 3.54) and 335 mμ ($\log \varepsilon$ 3.59). Infrared spectrum (nujol): 3480 (OH) and 1740 cm^{-1} (ester group).

Anal. Found: C, 67.46; H, 5.51. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21%.

From the above benzene filtrate, after removal of the solvent and crystallization from aqueous methanol, 100 mg. of methyl 2-methoxy-5-hydroxy-1-naphthyl acetate (VII), m. p. 146~149°C, was obtained. An analytical sample, obtained by recrystallization from a small amount of benzene, had m. p. 155.5~156.5°C.

Infrared spectrum[12]: 3400 (OH) and 1720 cm^{-1} (ester group).

Anal. Found: C, 68.15; H, 5.95. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73%.

Acetylation of the Tetralon Derivative (IV).—The keto acid (IV) (47 mg.) was added to a solution of acetic anhydride (0.5 cc.) in anhydrous pyridine (1.5 cc.) and the mixture was allowed to stand overnight. After concentration of the reaction mixture to a small volume, water and 2 N hydrochloric acid were added. The mixture was then shaken three times with ethyl acetate. The organic layers were combined, washed twice with water and dried over sodium sulfate. Removal of the solvent in vacuo left 33 mg. of an oily residue from which on trituration with petroleum ether, 24 mg. of crystalline material was obtained. For analysis the product was recrystallized from benzene, m. p. 176~176.5°C.

Ultraviolet absorption band at 276 mμ ($\log \varepsilon$ 4.22).

Anal. Found: C, 63.86; H, 4.67. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67%.

Dissociation constants of III and IV were measured at 25°C in 50% ethanol using HRL model M-3 pH meter.

Summary

1,2,3,4-Tetrahydro-5-hydroxy-1-naphthylacetic acid has been obtained from 2-methoxy-5-hydroxy-1-naphthylacetic acid by reduction either with sodium and *n*-butanol, or with lithium and liquid ammonia-ethanol. In the former case, under moderate conditions, 1,2,3,4-tetrahydro-2-oxo-4,5-dihydroxy-1-naphthylacetic acid has been isolated as a by-product.

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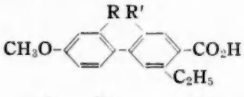
12) In the 1650~1500 cm^{-1} region, the dihydroxynaphthylacetate (VI) absorbs at 1630, 1608, 1590, 1524 cm^{-1}. See Ref. 1.

Estrogenic Biphenyls. VI[1]*. 2- and 6'-Alkyl Derivatives of 3'-Ethyl-4-methoxy-biphenyl-4'-carboxylic Acid*

By Takeo SATO and Michinori ŌKI*

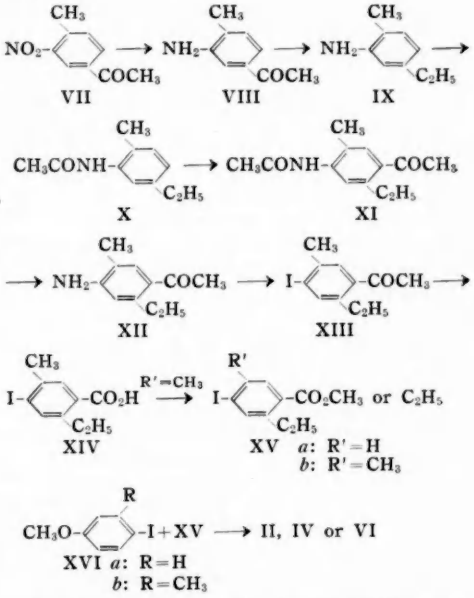
(Received March 16, 1959)

It was reported[2] that 3'-ethyl-4-methoxybiphenyl-4'-carboxylic acid (I) was fully estrogenic at the dose of 250 γ when injected subcutaneously to ovariectomized mice. Introduction of an additional ethyl group into position 2 or 6' of compound I increased the activity to a minimum active dose of 100 γ, thus 2,3'-diethyl-4-methoxybiphenyl-4'-carboxylic acid (III)[3] and 2',5'- (for 3',6')-diethyl-4-methoxybiphenyl-4'-carboxylic acid (V)[4] being the most active members of this series hitherto known. Enhancement of the estrogenic activity in compounds III and V in comparison with compound I was taken as an indication of a favorable molecular conformation in III and V as had already been observed in dialkylstilbestrol dimethyl ethers and related compounds[5]. The ethyl group introduced into position 2 or 6' was found to force the two benzene rings to a non-planar arrangement from the ultraviolet absorption spectra.



	R	R'		R	R'
I	H	H	IV	H	CH_3
II	CH_3	H	V	H	C_2H_5
III	C_2H_5	H	VI	CH_3	CH_3

The present communication deals with further studies on the effect of the 2- and 6'-alkyl substituents on the conformation and on the estrogenic activity of compound I and with the discussion on the relation between the physiological activity and the molecular structure in this series. 3'-Ethyl-4-methoxy-2-methylbiphenyl-4'-carboxylic acid (II) was prepared from 4-iodo-3-methylanisole (XVIb)[6] and ethyl 2-ethyl-4-iodobenzoate (XVa)[3] through the Ullmann reaction. The 6'-methyl isomer, namely, 5'-ethyl-4-methoxy-2'-methylbiphenyl-4'-carboxylic acid (IV), and the 2,6'-dimethyl derivative, namely, 5'-ethyl-4-methoxy-2,2'-dimethylbiphenyl-4'-carboxylic acid (VI), were prepared from methyl 2-ethyl-4-iodo-5-methylbenzoate (XVb) and the corresponding iodoanisoles (XVIa or b). The preparation of the ester XVb is shown in the accompanying diagram.



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1) Part V: T. Sato, This Bulletin, **32**, 1130 (1959).
2) T. Sato and M. Ōki, ibid., **30**, 958 (1957).
3) M. Ōki and T. Sato, ibid., **30**, 508 (1957).
4) M. Ōki and T. Sato, ibid., **30**, 702 (1957).
5) M. Ōki and Y. Urushibara, ibid., **25**, 109 (1952).
6) T. Sato and M. Ōki, ibid., **30**, 859 (1957).

Modified Wolff-Kishner reduction[7] of 3-amino-4-methylacetophenone (VIII)[8] afforded 5-ethyl-2-methylaniline (IX) in an excellent yield which was acetylated in the usual manner to give 5-ethyl-2-methylacetanilide (X). The acetanilide was treated with acetyl chloride and aluminum chloride in carbon disulfide and resulting 4-acetamido-2-ethyl-5-methylacetophenone (XI) was refluxed with dilute hydrochloric acid to give 4-amino-2-ethyl-

7) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946); **70**, 2802 (1948); **71**, 3301 (1949).
8) I. J. Rinkes, *Rec. trav. chim.*, **64**, 205 (1945).

5-methylacetophenone (XII). Diazotization of the aminoketone XII followed by treatment of the diazonium salt with potassium iodide yielded 2-ethyl-4-iodo-5-methylacetophenone (XIII), which was oxidized with sodium hypobromite to 2-ethyl-4-iodo-5-methylbenzoic acid (XIV). Esterification of compound XIV gave the desired ester XVb.

The ultraviolet absorption data of compounds II, IV and VI are recorded in Table I together with those of compounds I[6], III[4] and V[4]. Compounds II and IV showed the K-band at 272 and 270 mμ, respectively, approximately in the regular intensities characteristic of this system. Hypsochromic shift of some 15 mμ caused by the introduction of the methyl substituent into an ortho position to the pivot bond is the result of an increase in the interplanar angle of the two benzene nuclei to relieve the steric hindrance. The shift is, however, smaller by 2 mμ than in the corresponding compounds with the ethyl group (III and V), and it agrees with the data of the present authors[6] and others[9]. It is noteworthy that the 6'-alkyl derivative of compound I gives an absorption maximum at a shorter wavelength than the 2-alkyl derivative whether the alkyl is methyl or ethyl. The result is in good agreement with the idea of hyperconjugation of the alkyl group with the carboxyl group through the benzene nucleus, with which the 2-alkyl derivative is favored[10]. In the 2,6'-dimethyl derivative (VI), no K-band maximum was found in the region examined but a shoulder at ca. 270 mμ was noticed. This is undoubtedly caused by further deterioration in conjugation of the biphenyl skeleton.

TABLE I. ULTRAVIOLET ABSORPTION MAXIMA[a] AND ESTROGENIC ACTIVITIES OF 2- AND 6'-ALKYL DERIVATIVES OF 3'-ETHYL-4-METHOXYBIPHENYL-4'-CARBOXYLIC ACID

Compound	λ, mμ	log ε	Active dose in mice, γ
I	286	4.36	250
II	272	4.13	100
III	270	4.09	100
IV	270	4.17	100[c]
V	268	4.14	100
VI	~270[b]	3.92	500

a) In 95% ethanol. b) ~: Indicates a shoulder. c) Active in 80% animals.

9) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).
10) M. Ōki and H. Iwamura, unpublished work; also see Ref. 1.

The physiological data in Table I were obtained by the usual vaginal smear test with ovariectomized mice. The activities of the compounds with a methyl group were nearly the same as those with an ethyl group at the same position. The estrogenic potency is surely raised by the introduction of an alkyl group into position 2 or 6', but again no difference due to the change in the alkyl group was observed. Although the minimum active dose of compound VI to produce estrus in 100% animals was found to be 500 γ, it is not certain whether the excessive thickness of the molecule as indicated by the greater deterioration in conjugation really weakened the estrogenic activity of this compound, because it was active in 80% animals at 100 γ.

Experimental[11]

5-Ethyl-2-methylacetanilide (X).—A mixture of 149 g. (1 mol.) of 3-amino-4-methylacetophenone (VIII), obtained from 3-nitro-4-methylacetophenone (VII) according to Rinkes[8], 69 g. (1.1 mol.) of 80% hydrazine hydrate, 280 g. of potassium hydroxide and 1 kg. of diethylene glycol, was heated under reflux for two hours. Then the low boiling fraction was distilled off until the pot temperature reached 180°C. After the remaining mixture was refluxed for further three hours, the whole was steam-distilled and the distillate was combined with the low boiling fraction collected previously. The combined distillate was extracted with ether and the extract was dried over potassium carbonate. 5-Ethyl-2-methylaniline (IX) was obtained as a colorless liquid boiling at 78~79°C/3 mm. in 90% yield. The acetanilide X was obtained by acetylation with acetic anhydride, m. p. 136~137°C. The reported melting point is 138°C[8].

4-Acetamido-2-ethyl-5-methylacetophenone (XI).—To a well stirred suspension of 165 g. (0.93 mol.) of compound X in 78 g. (1 mol.) of acetyl chloride and 750 ml. of carbon disulfide, was added 415 g. (3.1 mol.) of anhydrous aluminum chloride in small portions in the course of one hour, while the mixture was gently refluxed. It was refluxed for another hour and then allowed to stand for two hours. The upper layer was decanted off and the viscous oil was decomposed with ice water and hydrochloric acid. The crystals were collected and recrystallized from aqueous ethanol to give 170 g. (79% yield) of colorless needles, m. p. 139~140°C.

Anal. Found: N, 6.56. Calcd. for $C_{13}H_{17}NO_2$: N, 6.39%.

4-Amino-2-ethyl-5-methylacetophenone (XII).—The acetamido compound XI was hydrolyzed with 1:1 aqueous hydrochloric acid. Colorless needles, m. p. 105~106°C, were obtained on recrystallization from benzene-petroleum ether.

11) All melting and boiling points are uncorrected.

Anal. Found: N, 8.22. Calcd. for $C_{11}H_{15}NO$: N, 7.91%.

2-Ethyl-4-iodo-5-methylacetophenone (XIII).—To a diazonium salt solution obtained from 32 g. (0.18 mol.) of compound XII, 39 ml. of concentrated sulfuric acid, 54 ml. of water and 13 g. (0.19 mol.) of sodium nitrite in a minimum quantity of water, was added a solution of 31 g. (0.19 mol.) of potassium iodide in a small amount of water. Stirring was continued for 30 min. at a low temperature and then at 50~60°C for two hours. The mixture was extracted with ether and the extract was washed with aqueous sodium hydroxide, aqueous sodium thiosulfate and water. The iodoacetophenone was obtained in a 50% yield as a brown oil boiling at 127~128°C/2.5 mm. On standing it solidified and colorless needles melting at 51~52°C were obtained on recrystallization from petroleum ether.

Anal. Found: I, 43.88. Calcd. for $C_{11}H_{13}IO$: I, 44.08%.

2,4-Dinitrophenylhydrazone.—It was obtained as orange needles, m. p. 165~166°C, on recrystallization from ethyl acetate.

Anal. Found: N, 11.54. Calcd. for $C_{18}H_{19}IN_4O_4$: N, 11.62%.

2-Ethyl-4-iodo-5-methylbenzoic Acid (XIV).—To a well stirred sodium hypobromite solution prepared from 28 g. (0.18 mol.) of bromine, 20 g. (0.50 mol.) of sodium hydroxide and 120 ml. of water, was added a solution of 17 g. (0.057 mol.) of compound XIII in 60 ml. of dioxan in one hour. The temperature was kept below 10°C during the addition and then at 50~60°C for one hour. After excessive hypobromite was decomposed with sodium sulfite, the whole was steam-distilled. The remaining solution was acidified with hydrochloric acid and the product was recrystallized from aqueous ethanol. Colorless needles, m. p. 157~158°C, were obtained in 90% yield.

Anal. Found: I, 44.41. Calcd. for $C_{10}H_{11}IO_2$: I, 43.77%.

Methyl 2-Ethyl-4-iodo-5-methylbenzoate (XVb).—The acid XIV was esterified in the usual manner. The ester, b. p. 125°C/2.5 mm., was obtained in a 78% yield.

Anal. Found: I, 42.08. Calcd. for $C_{11}H_{13}IO_2$: I, 41.76%.

3'-Ethyl-4-methoxy-2-methylbiphenyl-4'-carboxylic Acid (II).—With vigorous stirring 15 g. (0.24 atom) of copper bronze activated by Kleiderer and Adams' method[12] was added in small portions to a mixture of 9 g. (0.036 mol.) of 4-iodo-2-methylanisole (XVIb) and 5 g. (0.016 mol.) of ethyl 2-ethyl-4-iodobenzoate[3] over a period of 30 min., while the temperature was maintained at 215~220°C. The mixture was then heated to 280~285°C and was stirred for 30 min. at that temperature. After cooling, the whole was extracted with boiling acetone and the extract was refluxed with 40 ml. of 10% aqueous sodium hydroxide and 70 ml. of ethanol for two hours. A part of ethanol was removed by distillation and the residue was diluted with water to make up 500 ml. and an insoluble oil was removed by extraction with ether. The aqueous layer was acidified with hydrochloric acid and the acid mixture thus collected was extracted with hot benzene. On concentration of the solution it afforded a crude product, which on repeated recrystallization from aqueous ethanol gave 500 mg. of colorless needles melting at 150.5~151°C.

Anal. Found: C, 75.32; H, 6.80. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

5'-Ethyl-4-methoxy-2'-methylbiphenyl-4'-carboxylic Acid (IV).—The Ullmann reaction was carried out in the same way as described above with 15 g. (0.064 mol.) of 4-iodoanisole (XVIa), 9 g. (0.030 mol.) of methyl 2-ethyl-4-iodo-5-methylbenzoate (XVb) and 20 g. (0.32 atom) of activated copper bronze. The temperature for the addition of copper bronze was 230~240°C and then raised to 280~290°C. The acidic portion was digested with ether and the ethereal solution was passed through an alumina column. The elute was evaporated and repeated recrystallization of the residue from ethanol gave colorless needles melting at 188~189°C. It weighed 900 mg.

Anal. Found: C, 75.35; H, 6.51. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

5'-Ethyl-4-methoxy-2,2'-dimethylbiphenyl-4'-carboxylic Acid (VI).—The reaction was carried out in the same way as described for the preparation of II, with 18 g. (0.073 mol.) of compound XVIb, 10 g. (0.033 mol.) of compound XVb and 30 g. (0.47 atom) of activated copper bronze. The reaction temperatures were the same as in the preparation of IV. The acetone extract was distilled under reduced pressure to remove any unchanged materials, and the distillate up to 190°C/5 mm. was discarded. Colorless plates, melting at 127~128°C after recrystallization from ethanol-water, were obtained by handling the residue of vacuum distillation as described before. It weighed 600 mg.

Anal. Found: C, 76.27; H, 7.39. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were measured with a Hitachi photo-electric spectrophotometer Model EPU-2. The samples were dissolved in 95% ethanol.

The authors wish to express their hearty thanks to Professor Y. Urushibara, the University of Tokyo, and Professor K. Hata, Tokyo Metropolitan University, for encouragement throughout this work, and to the Research Department of Teikoku Hormone Manufacturing Co., Kawasaki, for bioassays. The authors' thanks are also due to the Ministry of Education for the Grant in Aid for Fundamental Research.

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12) E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, 55, 4219 (1933).

Estrogenic Biphenyls. VII. Preparation and Estrogenic Action of Methoxyl Derivatives of 4-Methoxybiphenyl-4'-carboxylic Acid

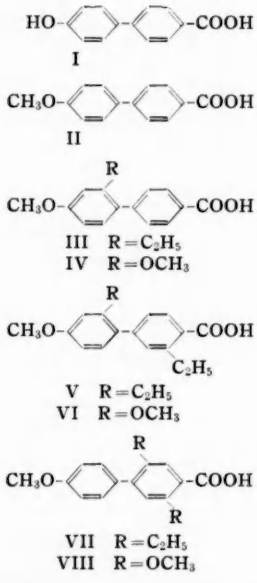
By Takeo SATO

(Received April 20, 1959)

In the study on the relation between the estrogenic activity and the molecular structure it has been found that in 4-hydroxybiphenyl-4'-carboxylic acid (I) and its methyl ether (II) the introduction of alkyl groups into suitable positions of the biphenyl skeleton increases the activity[1-6]. That the introduction of alkyl groups into position 2 or 2' of 4-methoxybiphenyl-4'-carboxylic acid (II) largely modifies the otherwise planar conformation of the biphenyl skeleton is apparent from the ultraviolet absorption spectra. The enhancement of the activity caused by the alkyl groups is explained on the basis of the steric effect of the alkyl groups, which makes the molecular structure or the conformation more suitable for the development of the physiological activity.

The minimum active doses of typical compounds of this series were found to be as follows: The parent compound II[3] was active only in 50% of ovariectomized mice at the dose of 1 mg., while full estrus was produced in 100% animals by a dose of 500 γ of compound III[3] and by 100 γ of either compound V[1] or compound VII[2]. The substances with a methyl or a propyl group in place of the ethyl group in compound III showed an activity similar to that of compound III in contrast to the case of the stilbene series[7]. This may be understood, when the similar ultraviolet absorption spectra of these homologous compounds are interpreted as the indication of their similar basic biphenyl skeletons which are not altered by the chain length of the straight-chain alkyl groups at position 2[2,3,8].

It was not explained, however, that the estrogenic activity of 2,2'-disubstituted



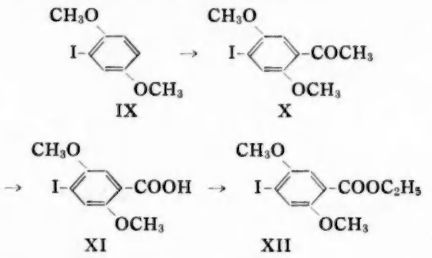
derivatives[5,6], whose ultraviolet spectra differed markedly from those of the monoalkyl derivatives in missing the characteristic K-band in the region examined, was nearly the same as that of the monoalkyl derivatives. The fact was striking because the physiological activity such as estrogenic activity is considered to be very sensitive even to a slight deformation of the structure.

In this connection it is interesting to prepare the alkoxyl analogues in which the alkoxyl group will take the same arrangement as alkyl groups but will produce less steric hindrance. The present communication describes the preparation of three such methoxyl analogues, IV, VI and VIII. The effect of the replacement of the alkyl group by the methoxyl group on the estrogenic activity may be compared with the case of the methoxyl analogues of hexestrol. Takahashi reported that 1, 2-dimethoxy-1,2-bis-(*p*-hydroxyphenyl)-ethane was fully active at 0.5 γ while the ethoxyl analogue was so at

1) M. Ōki and T. Sato, This Bulletin, **30**, 508 (1957).
2) M. Ōki and T. Sato, ibid., **30**, 702 (1957).
3) T. Sato and M. Ōki, ibid., **30**, 859 (1957).
4) T. Sato and M. Ōki, ibid., **30**, 958 (1957).
5) T. Sato, ibid., **32**, 1130 (1959).
6) T. Sato and M. Oki, ibid., **32**, 1289 (1959).
7) M. Oki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 252 (1952); M. Ōki and Y. Urushibara, This Bulletin, **25**, 109 (1952).
8) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).

10 γ[9]. The compound in which only one of the ethyl groups of hexestrol was replaced by a methoxyl group was less active than the dimethoxyl compound[10].

2,4-Dimethoxybiphenyl-4'-carboxylic acid (IV) was prepared by the Ullmann reaction of 2,4-dimethoxyiodobenzene and ethyl 4-iodobenzoate. The 2-methoxyl analogue (VI) of 2,3'-diethyl-4-methoxybiphenyl-4'-carboxylic acid (V), one of the most active members of the alkyl series, was prepared from 2,4-dimethoxyiodobenzene and ethyl 2-ethyl-4-iodobenzoate[1] through the same method. 2',4,5'-Trimethoxybiphenyl-4'-carboxylic acid (VIII), the totally methoxylated analogue of the diethyl compound VII, was obtained from 4-iodoanisole and ethyl 4-iodo-2,5-dimethoxybenzoate (XII), which was prepared by the following reaction sequence:



2,5-Dimethoxyiodobenzene (IX), prepared either from hydroquinone dimethyl ether by direct iodination or from 2,5-dimethoxyaniline by diazo reaction, was treated with acetyl chloride and aluminum chloride in carbon disulfide. 4-Iodo-2,5-dimethoxyacetophenone (X), thus produced, was oxidized with sodium hypobromite to give the corresponding benzoic acid XI, which was esterified to XII in the usual manner. Attempted Friedel-Crafts reaction of 2,5-dimethoxyacetanilide in carbon disulfide with the aim of obtaining 4-acetamido-2,5-dimethoxyacetophenone, which might be another intermediate for the preparation of XII, failed and the starting material was recovered.

The estrogenic activities were determined by the vaginal smear test with ovariectomized mice, substances in oil solution being injected subcutaneously. Compound IV was found active at 400 γ, while the corresponding ethyl compound (III) at 500 γ, as stated above. Compound VI was active only to 20% of the test animals at 100 γ, while the corresponding diethyl compound (V) was fully estrogenic at this level. The same situation is also observed in 2',5'-disubstituted compounds. Namely, while the 2',5'-diethyl compound (VII) was active equally to compound V, the 2',5'-dimethoxyl analogue (VIII) was active to 40% of the animals even at 200 γ. Although these 2-methoxyl compounds may be represented by thinner structural models than the corresponding alkyl compounds, the weaker activities of the former may be attributed to the thinner structures only with a reserve, since the direct physiological effect of the methoxyl group itself is obscure.

Experimental*

2,4-Dimethoxybiphenyl-4'-carboxylic Acid (IV).—With good stirring, 15 g. (0.057 mol.) of 2,4-dimethoxyiodobenzene, prepared by iodination of resorcinol dimethyl ether with iodine and yellow mercuric oxide according to Kauffmann and Kieser[11], and 5 g. (0.018 mol.) of ethyl 4-iodobenzoate were heated to 230°C and 15 g. (0.24 atom) of activated copper bronze[12] was added in small portions over a period of twenty minutes, while the temperature was maintained at 230~250°C. When the addition was over, the reaction mixture was heated to 280~290°C and kept at that temperature for thirty minutes. The acetone extract was subjected to vacuum distillation and the distillate up to 120°C/5 mm. was discarded. The residue was hydrolyzed with aqueous-alcoholic alkali and tetramethoxybiphenyl was removed by filtration. Acidification of the aqueous solution gave a crude product, which was extracted with hot acetic acid, and the substance obtained from the extract was recrystallized from ethanol to yield 1 g. of colorless plates melting at 199~200°C.

Anal. Found: C, 69.39; H, 5.99. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%.

3'-Ethyl-2,4-dimethoxybiphenyl-4'-carboxylic Acid (VI).—In the same way as described for the preparation of compound IV, 11 g. (0.042 mol.) of 2,4-dimethoxyiodobenzene and 5.5 g. (0.018 mol.) of ethyl 2-ethyl-4-iodobenzoate[1] were condensed with 15 g. (0.24 atom) of activated copper bronze. The acetone extract was concentrated until the temperature of the distilling vapor reached 152°C at 5 mm. The crude acid, obtained by hydrolysis of the product, was extracted with hot benzene. Repeated recrystallization from ethanol gave 200 mg. of colorless needles melting at 187~187.5°C.

Anal. Found: C, 71.24; H, 6.10. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

9) T. Takahashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 765 (1952); Y. Urushibara and T. Takahashi, This Bulletin, **23**, 53 (1950).
10) T. Takahashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 629 (1952).

* All boiling and melting points are uncorrected. The author is indebted to Mr. T. Mizushima for carrying out the microanalyses.
11) H. Kauffmann and F. Kieser, *Ber.*, **45**, 2333 (1912).
12) E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, **55**, 4219 (1933).

2,5-Dimethoxyiodobenzene. — Hydroquinone dimethyl ether was iodinated with iodine and mercuric oxide[13]. It was also prepared[14] from 2,5-dimethoxyaniline by diazotization followed by decomposition in the presence of potassium iodide.

4-Iodo-2, 5-dimethoxyacetophenone (X).—To a well stirred mixture of 100 ml. of carbon disulfide and about one fifth of 33 g. (0.25 mol.) of powdered aluminum chloride was added dropwise a solution consisting of 16 g. (0.20 mol.) of acetyl chloride and 50 g. (0.19 mol.) of 2, 5-dimethoxyiodobenzene in the course of thirty minutes, while the rest of the aluminum chloride was added occasionally through another opening of the flask. The reaction mixture was gently refluxed for one hour and then poured into ice water containing hydrochloric acid. The carbon disulfide layer was concentrated and the residue was extracted with ether. The ethereal solution was successively washed with water, aqueous alkali, sodium thiosulfate and again water. Evaporation of the solution afforded 15 g. (26% of the theoretical) of light brown needles melting at 98~99°C on recrystallization from ethanol.

Anal. Found: C, 39.28; H, 3.60. Calcd. for $C_{10}H_{11}O_3I$: C, 39.23; H, 3.62%.

The 2, 4-Dinitrophenylhydrazone was obtained as deep-orange plates, m. p. 210~212°C, on recrystallization from ethyl acetate.

Anal. Found: N, 11.72. Calcd. for $C_{16}H_{15}O_6N_4I$: N, 11.53%.

4-Iodo-2, 5-dimethoxybenzoic Acid (XI).—To a sodium hypobromite solution, prepared by dropping 21 g. (0.13 mol.) of bromine into 15 g. (0.38 mol.) of sodium hydroxide in 130 ml. of water below 0°C, was added 14 g. (0.046 mol.) of compound X dissolved in 50 ml. of dioxan over a period of one hour, the temperature being kept below 20°C. After the excessive hypobromite was decomposed with sodium bisulfite, the whole was steam-distilled and the remainder was acidified with hydrochloric acid. Colorless needles melting at 175~177°C were obtained on recrystallization of the product from ethanol. Yield, 10 g. or 71% of the theoretical.

Anal. Found: C, 35.25; H, 3.00. Calcd. for $C_9H_9O_4I$: C, 35.09; H, 2.94%.

Ethyl 4-Iodo-2, 5-dimethoxybenzoate (XII).—A solution of 5 g. (0.016 mol.) of compound XI in 50 ml. of ethanol, saturated with dry hydrogen chloride, was heated under reflux for five hours. After the solvent was removed the residue was diluted with water and extracted with ether. The ethereal solution was successively washed with water, sodium bicarbonate solution, sodium thiosulfate solution and again water. Colorless plates melting at 65~66°C were obtained on recrystallization from petroleum ether. Yield, 5 g. or 93% of the theoretical.

Anal. Found: C, 39.30; H, 3.95. Calcd. for $C_{11}H_{13}O_4I$: C, 39.30; H, 3.90%.

2', 4, 5'-Trimethoxybiphenyl-4'-carboxylic Acid (VIII).—The Ullmann reaction was carried out in the same way as described for the preparation of compound IV, using 8 g. (0.034 mol.) of 4-iodoanisole, 5 g. (0.015 mol.) of compound XII and 15 g. (0.24 atom) of activated copper bronze. The acidic part was extracted with hot benzene and the extract was concentrated to yield 200 mg. of colorless plates melting at 142~143°C.

Anal. Found: C, 66.84; H, 5.48. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59%.

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13) H. Kauffmann and I. Fritz, *Ber.*, **41**, 4413 (1908).
14) F. Ullmann et al., *Ann.*, **332**, 38 (1904).

Synthesis and Physical Properties of Normal Higher Alcohols. I. Synthesis of Normal Higher Primary Alcohols of Odd Carbon Numbers from Undecanol to Pentacosanol

By Akira WATANABE*

(Received March 17, 1959)

As part of a broad program of investigating the synthesis and physical properties of long chain compounds, the present author has taken up normal primary alcohols. Since Müller[1] reported an X-ray investigation of a series of normal paraffins, a phenomenon of phase transitions in the solid state of long chain compounds has drawn much attention of chemists and physicists.

Although several communications dealing with the transition phenomenon of long chain compounds have appeared in the literature, higher alcohols have not been studied as fully as paraffins and consequently the results are rather fragmentary and somewhat ambiguous. Moreover, only few reports are found on the alcohols with odd carbon numbers and more than eighteen carbon atoms[2]. A reason for this may have been the difficulty of obtaining a series of higher alcohols in high purity. Therefore, it is desirable to investigate in more detail and more systematically the synthesis and the physical properties of the series of alcohols. From this point of view, the author has undertaken to synthesize alcohols having more than ten carbon atoms and in this paper the preparation of higher alcohols of odd carbon numbers from undecanol $C_{11}H_{23}OH$ to pentacosanol $C_{25}H_{51}OH$ is reported.

Until recently, all the alcohols up to hexatriacontanol $C_{36}H_{73}OH$ have been synthesized by other workers for the purpose of making comparison with naturally occurring products. In the present investigation, the three synthetic routes were chosen depending upon the availability of starting materials and close attention was paid to obtain the products having sufficient purity for physical studies.

(A) $RCO_2H \rightarrow RCO_2Ag \xrightarrow[(\text{in } CCl_4)]{Br_2} RBr \xrightarrow{CH_3CO_2Ag} CH_3CO_2R \xrightarrow{H_2O} ROH$

(B) $RCO_2H \xrightarrow{SOCl_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow[(\text{in } CH_3OH)]{Ag_2O} RCH_2CO_2CH_3 \xrightarrow{LiAlH_4} RCH_2CH_2OH$

(C) $C_2H_5O_2C(CH_2)_5Br \xrightarrow{\text{Ethyl malonate}}$

(I)

$C_2H_5O_2C(CH_2)_5CH(CO_2C_2H_5)_2 \xrightarrow[Na]{C_6H_5CH_2OH}$

(II)

$C_6H_5CH_2O_2C(CH_2)_5CNa(CO_2CH_2C_6H_5)_2 \xrightarrow{RCOCl}$

(III)

$C_6H_5CH_2O_2C(CH_2)_5C(CO_2CH_2C_6H_5)_2COR \xrightarrow[2.-CO_2]{1.\ H_2}$

(IV)

$RCO(CH_2)_6CO_2H \xrightarrow{\text{Huang-Minlon reduction}}$

(V)

$R(CH_2)_7CO_2H \rightarrow R(CH_2)_7CO_2C_2H_5$

(VI) (VII)

$\xrightarrow{LiAlH_4} R(CH_2)_9OH$

(VIII)

Undecanol $C_{11}H_{23}OH$, tridecanol $C_{13}H_{27}OH$, pentadecanol $C_{15}H_{31}OH$, heptadecanol $C_{17}H_{35}OH$ and heneicosanol $C_{21}H_{43}OH$ were prepared by method A. The process of degradative bromination of silver salts of fatty acids is the well known Hunsdiecker reaction[3]. The alkyl bromides obtained by this method were heated with silver acetate at 150°C without a solvent to yield the acetyl compounds which were converted into the desired alcohols by hydrolysis with alcoholic potassium hydroxide. Overall yields were about 40%.

Nonadecanol $C_{19}H_{39}OH$ was prepared by the Arndt-Eistert reaction (method B) from stearic acid. Stearoyl chloride, obtained from stearic acid and thionyl chloride, and diazomethane in ether gave

* Some parts of this work were perfomed of Department of Chemisty, Faculty of Science, Kyoto University Sakyo-ku, Kyoto.

1) A. Müller, *Proc. Roy. Soc.*, **A138**, 514 (1932).

2) Review of the literature is presented in a paper by Kakiuchi et al., *J. Phys. Soc. Japan*, **75**, 291 (1950).

3) H. Hunsdiecker and Cl. Hunsdiecker, *Ber.*, **75**, 291 (1942).

TABLE I. ALCOHOLS

Alcohols	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H	m. p.*, °C	t. p.**, °C
Undecyl	$C_{11}H_{24}O$	76.67	14.04	76.55	13.19	14.0	14.3[a] —
Tridecyl	$C_{13}H_{28}O$	77.93	14.09	77.80	13.93	30.5	30.5[b] 27.7
Pentadecyl	$C_{15}H_{32}O$	78.87	14.12	79.11	14.17	45.0	45.0[c] 38.0
Heptadecyl	$C_{17}H_{36}O$	79.61	14.15	79.47	14.23	54.0	54.0[d] 46.0
Nonadecyl	$C_{19}H_{40}O$	80.20	14.17	80.38	14.12	62.5	63.0[e] 51.0
Heneicosyl	$C_{21}H_{44}O$	80.69	14.19	80.53	14.10	69.0	69.0[e] 55.0
Tricosyl	$C_{23}H_{48}O$	81.10	14.20	81.30	14.14	72.5	73.1[f] 63.0
Pentacosyl	$C_{25}H_{52}O$	81.44	14.21	81.45	14.16	77.5	77.3[f] 68.0

* Melting points are uncorrected.

** When a sample is cooled below its freezing point, transition appears with change of the transparent waxy material into an opaque crystalline state.

a) R. Robinson, *J. Chem. Soc.*, **125**, 229 (1924).
b) J. Blau, *Monatshe. Chem.*, **26**, 106 (1905).
c) E. Jeffreys, *Am. Chem. J.*, **22**, 28 (1899).
d) P. A. Leven et al., *J. Boil. Chem.*, **20**, 531 (1915).
e) P. A. Leven et al., ibid., **59**, 915 (1924).
f) S. Shiina, *J. Soc. Chem. Ind., Japan* (*Kōgyō Kwagaku Zassi*), **39**, 345 (1936).

TABLE II. FATTY ACIDS

Acids	m. p., °C	Acid value Expt.	Acid value Calcd.	Iodine value	Methyl esters m. p., °C	Methyl esters b. p., °C
Lauric	43.0	279.0	280.2	0	—	110/4 mm.
Myristic	53.5	244.2	245.8	0	18.0	140/4 mm.
Palmitic	62.3	218.6	219.0	0.02	29.0	160/5 mm.
Stearic	69.6	196.5	197.4	0	38.5	178/4 mm.
Behenic	79.5	164.0	164.9	0.1	48.0*	185/1.8 mm.

* Ethyl ester.

diazononadecanone which had been synthesized by Grundmann previously[4]. The conversion of the diazoketone into methyl nonadecanoate with silver oxide in methanol was carried out easily. The ester was reduced with lithium aluminum hydride to nonadecanol in almost quantitative yield.

Method C which was used for the synthesis of tricosanol $C_{23}H_{47}OH$ and pentacosanol $C_{25}H_{51}OH$ is analogous to that of Bowman's ketone synthesis[5]. Ethyl *n*-hexane-1,1,6-tricarboxylate (II) which served as the starting material was prepared from ethyl malonate and ethyl bromocaproate which was obtained from cyclohexanone by the method of Brown[6]. Benzyl *n*-hexane-1,1,6-tricarboxylate derived from the ethyl ester by transesterification with benzyl alcohol was condensed with palmitoyl chloride or stearoyl chloride, to give, after hydrogenation and decarboxylation, 8-ketotricosanoic acid or 8-ketopentacosanoic acid. Reduction to the corresponding fatty acid by Huang-Minlon's method[7] was efficient. Ethyl tricosanoate and ethyl pentacosanoate were readily reduced to the desired alcohols with lithium aluminum hydride.

The physical constants and analytical data of the alcohols are given in Table I together with those reported by other workers who had previously synthesized them by different methods. The transition points of C_{19}, C_{21}, C_{23}, C_{25} alcohols were unknown.

Since it is known that sometimes minor impurities, especially homologues, have a marked influence on the transition behavior of long chain compounds, it was felt necessary to obtain the starting fatty acids in high purity. Commercial fatty acids such as lauric, myristic, palmitic, stearic,

4) C. Grundmann, *Ann.*, **524**, 37 (1936).
5) R. E. Bowman, *J. Chem. Soc.*, **1950**, 174.
6) G. B. Brown and C. W. H. Partridge, *J. Am. Chem. Soc.*, **66**, 839 (1944).
7) Huang-Minlon, ibid., **68**, 2487 (1946).

and behenic acids were obtained in a pure state by fractionation of the methyl ester through four feet Fenske column followed by saponification and recrystallization. Physical constants and analytical data of these fatty acids are given in Table II.

Experimental

Undecanol, Tridecanol, Pentadecanol, Heptadecanol and Heneicosanol.—These alcohols were prepared from the corresponding fatty acids by method A involving Hunsdiecker's reaction[3]. A typical example is given for the preparation of heneicosanol.

Silver behenate: $C_{21}H_{43}CO_2Ag$—A solution of 20 g. of potassium behenate in 200 ml. of ethanol was stirred on a steam bath while a solution of 13 g. of silver nitrate in 50% aqueous ethanol was added dropwise. The resulting bulky white precipitate was collected on a filter, thoroughly washed four times by suspension in 500 ml. of hot water, air-dried, and brought to complete dryness at 150°C under reduced pressure (2 mm.). The yield was almost quantitative.

Heneicosyl bromide: $C_{21}H_{43}Br$—The reaction was carried out under strict exclusion of moisture. To a suspension of 12 g. of silver behenate in 80 ml. of carbon tetrachloride was added a solution of 10 g. of bromine in 50 ml. of carbon tetrachloride which had previously been dried over phosphorus pentoxide. Reaction began immediately, with the evolution of carbon dioxide. When the reaction almost ceased, the reaction mixture was heated at the boiling point for a short period to complete the reaction. Silver bromide formed was filtered off and the solution was washed successively with water, sodium thiosulfate solution, 5% sodium hydroxide solution, and water, and dried over sodium sulfate. Evaporation of the solution gave 8.5 g. of an oily product, which solidified on standing at room temperature. Recrystallization from ethanol yielded the pure bromide which melted at 44.5～45°C and weighed 5.3 g. (53%).

Anal. Found: C, 67.5; H, 11.49. Calcd. for $C_{21}H_{43}Br$: C, 67.2; H, 11.47%.

The melting point is higher than that of docosyl bromide $C_{22}H_{45}Br$ (44°C)[3]. This is consistent with the fact that the melting points of normal alkyl bromides of odd carbon numbers are slightly higher than those of next higher homologue.

Heneicosanol: $C_{21}H_{43}CH$ — An intimate mixture of 5 g. of heneicosyl bromide and 2.3 g. of silver acetate was kept at 150°C for 3 hr. The reaction mixture was extracted three times with hot benzene. The benzene solution free from silver bromide was washed with water and dried over sodium sulfate. Evaporation of the solution gave 4.2 g. of a residue which was saponified without purification. The crude ester was refluxed for 3 hr. with 10 ml. of 30% alcoholic potassium hydroxide. The resulting alcohol was recrystallized twice from ethanol and twice from benzene to give heneicosanol in platelets, m. p. 68.5～69°C. Overall yield was 40% (3 g.).

Nonadecanol. — The intermediate diazoketone was prepared by the method of Grundmann[4]. The melting point of this compound was 69～70°C (reported 69°C).

Methyl nonadecanoate: $C_{18}H_{37}CO_2CH_3$—A slurry of freshly prepared silver oxide in methanol was added portionwise to a stirred solution of 18 g. of 1-diazo-2-nonadecanone in 160 ml. of methanol which was heated beforehand at 65°C. The addition required about 4 hr. and the temperature of the reaction mixture was kept at 60～65°C during the course of the reaction. At the end of this period a 2 ml. portion was taken from the solution and added to concentrated hydrochloric acid. An evolution of nitrogen was not observed, and then the solution was cooled and filtered. Partial removal of the methanol and subsequent cooling gave a white solid which was recrystallized from methanol, m. p. 42～43°C. The yield was 17 g. (95%). It was identified by the mixed melting point with an authentic sample.

Reduction of methyl nonadecanoate.—To a stirred suspension of 0.2 g. of lithium aluminum hydride in 25 ml. of dry ether was added a solution of 3 g. of methyl nonadecanoate in 15 ml. of ether dropwise at such a rate that a gentle reflux of the solvent was maintained. After the addition was complete, the solution was refluxed for 15 min. The excess of lithium aluminum hydride was decomposed by cautious addition of water and the reaction mixture was acidified with dilute sulfuric acid. The ether layer was removed, and washed with water to neutral reaction. The solid residue, obtained by removal of the solvent from the dried solution, was recrystallized four times from benzene to give nonadecanol in platelets, m. p. 62～62.5°C. Yield was 90% (2.3 g.).

Tricosanol. — The preparation of intermediate ethyl ε-bromocaproate (I) was modelled after that of Brown and Partridge[6]. From 50 g. of purified cyclohexanone 52 g. of the bromoester was obtained, b. p. 118°C/14 mm. or 98°C/4.5 mm., n_D^{30} 1.4561 (reported: b. p. 120～125°C/14 mm., n_D^{21} 1.4566).

Ethyl n-hexane 1,1,6-tricarboxylate (II).—The bromoester (33 g.) was refluxed with a solution of 48 g. of sodiomalonic ester in 150 ml. of absolute ethanol for 8 hr. After removal of the solvent the cooled mixture was treated with dilute solfuric acid and the triethylester was isolated in a usual manner as a colorless liquid, b. p. 150～151°C/1 mm. Yield, 28 g. (63%). n_D^{28}, 1.4360.

Anal. Found: C, 59.91; H, 9.01; Calcd. for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67%.

8-Ketotricosanoic acid (V): $CH_3(CH_2)_{14}CO(CH_2)_6CO_2H$—In a 200 ml. three-necked flask equipped with a mechanical stirrer, a dropping funnel and a reflux condenser fitted with a calcium chloride tube, were placed 0.75 g. of finely powdered sodium sand and 70 ml. of dry benzene. To the mixture was added from the dropping funnel 11.3 g. of ethyl *n*-hexane-1,1,6-tricarboxylate.

8) V. Braun et at., *Ann.*, 472, 132 (1929).

The mixture was refluxed with stirring until the sodium sand disappeared. It required about 8 hr. After 7.5 g. of benzyl alcohol (purified by oximation followed by distillation: b. p. 79~80°C/7 mm., odorless) was added, the reflux condenser was replaced by a Fenske column and the mixture was heated to distill off ethanol as the benzene-ethanol azeotrope. Then the Fenske column was again replaced by the reflux condenser. Palmitoyl chloride (9 g.) b. p. 148°C/1.5 mm. was added with stirring, and the resulting solution was refluxed for 1 hr. The neutral solution obtained was distilled under reduced pressure to give a yellow oil which could not be crystallized and was subjected to hydrogenation without purification. A solution of 25 g. of tribenzyl compound IV in 50 ml. of ethyl acetate was shaken with Pd-C (0.5 g.) and Pd-$SrCO_3$ (0.5 g.) in a hydrogen atmosphere of slightly positive pressure. After 10 hr. the absorption of hydrogen ceased, but during this period the fresh catalyst was added from time to time because of its poisoning, the total amount of catalyst being 4 g. The solution freed from the catalyst was refluxed for 30 min. to decarboxylate the product. After the solvent was partially removed, white small crystals separated out from the cooled solution. Repeated recrystallization from acetone gave white crystals having the constant melting point of 93.5~94°C. Yield was 23% (2.8 g.).

Anal. Found: C, 75.16; H, 12.00. Calcd. for $C_{23}H_{44}O_3$: C, 74.94; H, 12.03%.

Tricosanoic acid (VI): $C_{22}H_{45}CO_2H$—To a solution of 2.5 g. of potassium hydroxide in 30 ml. of diethylene glycol was added 2.5 g. of the ketonic acid and 2.5 ml. of hydrazine hydrate. The mixture was heated to 165°C in an oil bath. After 1 hr. of heating the water formed distilled off through a take-off condenser. The contents of the flask were held at 200°C for 6 hr., and cooled. The fatty acid was isolated by pouring the reaction mixture into an equal volume of water followed by acidification with dilute sulfuric acid. Recrystallization from benzene gave 2.2 g. of platelets, m. p. 78.5°C (reported: 79~79.3°C[9]). The ethyl ester of the acid was obtained by the usual method and purified by vacuum distillation followed by recrystallization from benzene, m. p. 51~52°C (reported: 51.2~51.4°C[9]), b. p. 207°C/1.5 mm.

Tricosanol: $C_{23}H_{47}OH$ — From 2 g. of ethyl tricosanoate, 0.15 g. of lithium aluminum hydride in absolute ether was obtained 1.3 g. of the pure alcohol which melted at 72.5°C.

Pentacosanol.—It was prepared analogously to tricosanol stearic acid, being used in place of palmitic acid. The experimental results are given briefly.

Condensation product of benzyl n-hexane-1,1,6-tricarboxylate with stearoyl chloride. — From 17 g. of the tribenzyl compound and 11 g. of stearoyl chloride (b. p. 169°C/1.5 mm.) were obtained 24 g. of a crude product in a state of viscous brown liquid.

8-Ketopentacosanoic acid: $CH_3(CH_2)_{16}CO(CH_2)_6CO_2H$—From 24 g. of the above benzyl compound, 2.5 g. of the ketonic acid was obtained. The product was recrystallized from acetone and then from benzene to a constant melting point of 97°C.

Anal. Found: C, 75.91; H, 12.05. Calcd. for $C_{25}H_{48}O_3$: C, 75.70; H, 12.20%.

Pentacosanoic acid: $C_{24}H_{49}CO_2H$ — The Huang-Minlon reduction of 2.5 g. of the ketonic acid gave 2.2 g. of pentacosanoic acid, m. p. 83.1°C (reported: 83.2~83.4°C[9]). Ethyl pentacosanoate, m. p. 57~58°C (reported: 57.1~57.4°C[9]), b. p. 215°C/0.7 mm.

Pentacosanol: $C_{25}H_{51}OH$ — By use of lithium aluminum hydride (0.15 g.), 1.7 g. of the pure product was obtanied from 2.1 g. the ethyl pentacosanoate. m.p. 77.5°C (from ligroin).

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9) S. Shiina, *J. Soc. Chem. Ind., Japan* (*Kôgyô Kwagaku Zassi*), **39**, 345 (1936).

Competitive Hydrogenation of Acetylenic Compounds

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1,4-Butynediol can be partially hydrogenated on the Pd-$CaCO_3$ catalyst, with quinoline as a poison, and also on the Pd-$BaCO_3$ catalyst poisoned by lead acetate and quinoline, but not on the ordinary palladium catalyst[1,2]. The effect of lead acetate on the Pd-$CaCO_3$ catalyst was different from that of quinoline. It was explained that lead acetate is adsorbed more strongly than 1,4-butynediol or 1,4-butenediol, while quinoline is adsorbed in competition with 1,4-butynediol and 1,4-butenediol[3].

It seems to be an interesting problem to study in more detail how the properties of the Pd-$CaCO_3$ catalyst are affected by such an additive as quinoline. Thus, the properties of the catalyst for the hydrogenation of phenylacetylene and propargyl alcohol were studied.

Experimental

Procedure. — The hydrogenation experiments were carried out with Pd-$CaCO_3$ catalyst[4] (Pd-content, 5% by wt.), at 25°C and at the atmospheric pressure in methyl alcohol. Phenylacetylene was prepared according to J. C. Hessler[5], and propargyl alcohol was a commercial product[6]. These were purified by distillation. The hydrogenation products were analyzed by gas chromatography.

The gas chromatography experiments were carried out at 100°C by a glass gas chromatography apparatus[7]. Polyethyleneglycol-400 column (P.E.G.-column) and polyethyleneglycol-400-dinonyl phthalate column (P.E.G.-D.N.P-column) were used. With P.E.G.- and P.E.G.-D.N.P.-columns, phenylacetylene, styrene, ethylbenzene, propargyl alcohol, allyl alcohol, and propyl alcohol eluted as shown in Fig. 1.

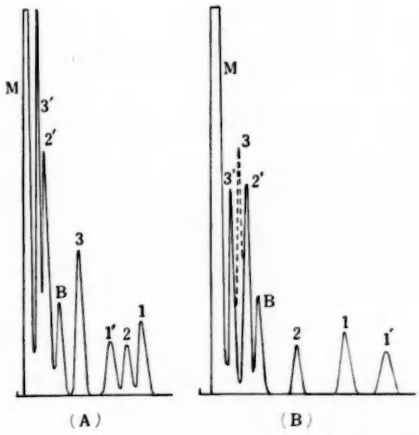

Fig. 1. Chromatogram on P.E.G-D.N.P-column and P.E.G.-column, at 100°C.
(A) P.E.G-D.N.P-column : [P.E.G-400-(20%)-celite : D.N.P (20%)-celite =9 : 12 (by wt.)]
length : 2 m., diameter : 4 mm.
(B) P.E.G-column : [P.E.G-400-(20%)-celite] length : 1 m., diameter : 4 mm.
carrier gas : H_2 (50 cc/min.)
1 : Phenylacetylene
2 : Styrene
3 : Ethylbenzene
1' : Propargyl alcohol
2' : Allyl alcohol
3' : Propyl alcohol
B : *n*-Butyl alcohol
M : Methyl alcohol

Results

The hydrogenation of phenylacetylene and propargyl alcohol on the Pd-$CaCO_3$ catalyst took place as shown in Fig. 2. It was shown that phenylacetylene and propargyl alcohol could not be partially hydrogenated in the presence of quinoline.

When 20 millimol. of phenylacetylene or propargyl alcohol in a concentration of 2 millimol./ml. was used, the reaction products were shown in Fig. 3. In these experiments, a mixture of methyl alcohol

1) T. Fukuda and T. Kusama, This Bulletin, **31**, 339 (1958).
2) T. Fukuda, ibid., **31**, 343 (1958).
3) T. Fukuda, ibid., **32**, 420 (1959).
4) H. Lindler, *Helv. Chim. Acta*, **30**, 1911 (1947).
5) J. C. Hessler, "Organic Syntheses", Col. Vol. 1, John Wiley & Sons, Inc., New York, p. 428.
6) A commercial extra pure grade (Tokyo Kasei Co., Tokyo).
7) T. Fukuda, *Japan Analyst* (*Bunseki Kagaku*), **8**, 627 (1959).

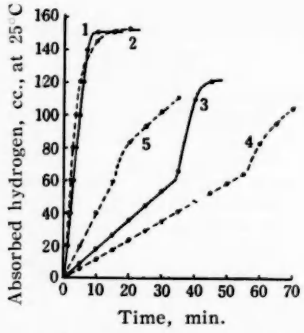

Fig. 2. The absorption of hydrogen in the hydrogenation of phenylacetylene and propargyl alcohol.
Pd-CaO_3 catalyst 100 mg.
1: Phenylacetylene (ca. 3.6 millimol.) ···methyl alcohol solution (20 cc.)
2: Phenylacetylene (ca. 3.6 millimol.) ···methyl alcohol-quinoline solution (20 cc.)
3: Propargyl alcohol (ca. 2.8 millimol.) ···aqueous solution (20 cc.)
4: Propargyl alcohol (ca. 2.8 millimol.) ···water-quinoline solution (20 cc.)
5: Propargyl alcohol (ca. 2.8 millimol.) ···quinoline solution (20 cc.)

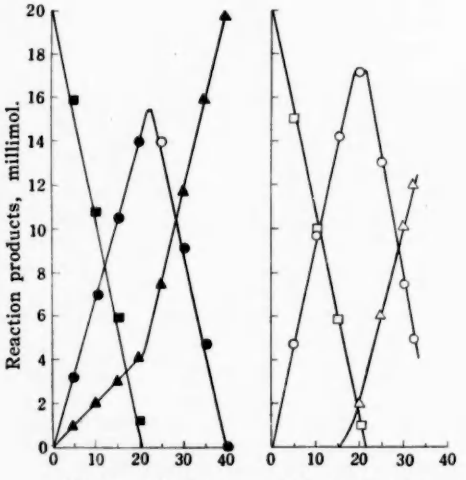

Fig. 3. The reaction products in the hydrogenation of phenylacetylene and propargyl alcohol.
Pd-$CaCO_3$ catalyst 1.00 g.
■ Phenylacetylene □ Propargyl alcohol
● Styrene ○ Allyl alcohol
▲ Ethylbenzene △ Propyl alcohol

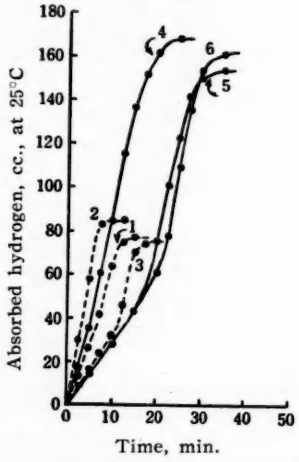

Fig. 4. The absorption rate of hydrogen in the competitive hydrogenation of acetylenic compounds.
Pd-$CaCO_3$ catalyst 100 mg.
Methyl alcohol solution (20 cc.)
1: 1,4-Butynediol (2 millimol.)
2: Phenylacetylene (2 millimol.)
3: Propargyl alcohol (2 millimol.)
4: Phenylacetylene (2 millimol.) +1,4-butynediol (2 millimol.)
5: Propargyl alcohol (2 millimol.) +1,4-butynediol (2 millimol.)
6: Phenylacetylene (2 millimol.) +propargyl alcohol (2 millimol.)

and *n*-butyl alcohol (an internal standard for the gas chromatographic analysis) was used as a solvent. The hydrogenation of phenylacetylene took place with simultaneous hydrogenation of about 20 mol. % of styrene. On the other hand, in the hydrogenation of propargyl alcohol, allyl alcohol was scarcely hydrogenated.

The competitive hydrogenation took place as shown in Fig. 4. When the concentration of the each acetylenic compound was 2 millimol./ml., the reaction products came out as shown in Figs. 5—7, with the absorbed amount of hydrogen. In these experiments, a mixture of methyl alcohol and *n*-butyl alcohol was used as a solvent. The peak of 1,4-butynediol, 1,4-butenediol, and 1,4-butanediol did not appear under the experimental conditions of the gas chromatography. However, the contents of these substances in the product could be roughly estimated from the absorbed amount of hydrogen as shown by the dotted lines, assuming that 1,4-butynediol and 1,4-butenediol were hydrogenated selectively.

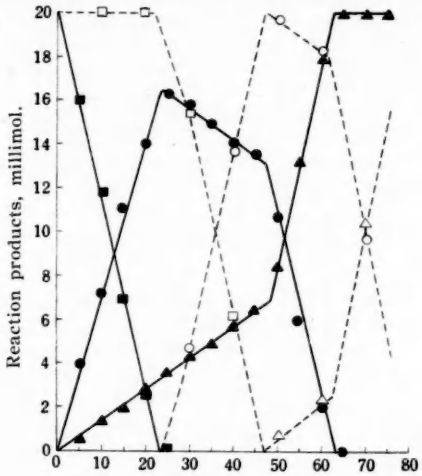

Fig. 5. The reaction products in the competitive hydrogenation of phenylacetylene and 1,4-butynediol.
$Pd\text{-}CaCO_3$ catalyst 1.00 g.
Phenylacetylene (20 millimol.)
1,4-Butynediol (20 millimol.)
■ Phenylacetylene □ 1,4-Butynediol
● Styrene ○ 1,4-Butenediol
▲ Ethylbenzene △ 1,4-Butanediol

It was shown that, in the competitive hydrogenation of 1,4-butynediol and phenylacetylene, the latter was hydrogenated first and the former was then hydrogenated, and both steps were accompanied by the hydrogenaion of a small amount of styrene.

The hydrogenation of 1,4-butenediol took place after that of styrene was completed. In the competitive hydrogenation of 1,4-butynediol and propargyl alcohol, the latter was hydrogenated first, and the hydrogenation of 1,4-butynediol with a small amount of allyl alcohol followed. The remaining allyl alcohol was hydrogenated with 1,4-butenediol. In the competitive hydrogenation of phenylacetylene and propargyl alcohol, the latter was hydrogenated with about 35 mol. % of the former. The remaining phenylacetylene was hydrogenated with a small amount of styrene and allyl alcohol. Styrene was hydrogenated with allyl alcohol.

Even when 0.2 millimol./ml. of phenylacetylene (or propargyl alcohol) and 1.8 millimol./ml. of 1,4-butynediol were used, the competitive hydrogenation took place similarly as explained above.

It was observed that an appreciable amount of allyl alcohol was consumed by

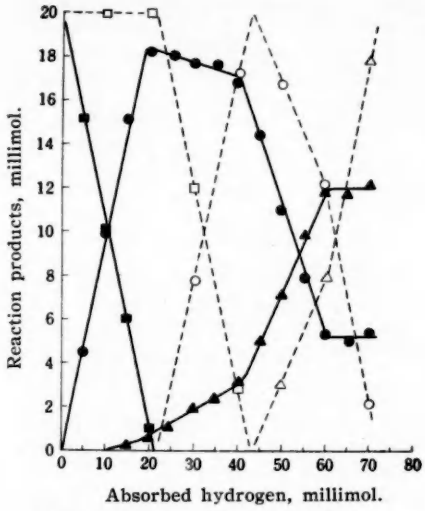

Fig. 6. The reaction products in the competitive hydrogenation propargyl alcohol and 1,4-butynediol.
$Pd\text{-}CaCO_3$ catalyst 1.00 g.
Propargyl alcohol (20 millimol.)
1,4-Butynediol (20 millimol.)
■ Propargyl alcohol □ 1,4-Butynediol
● Allyl alcohol ○ 1,4-Butenediol
▲ Propyl alcohol △ 1,4-Butanediol

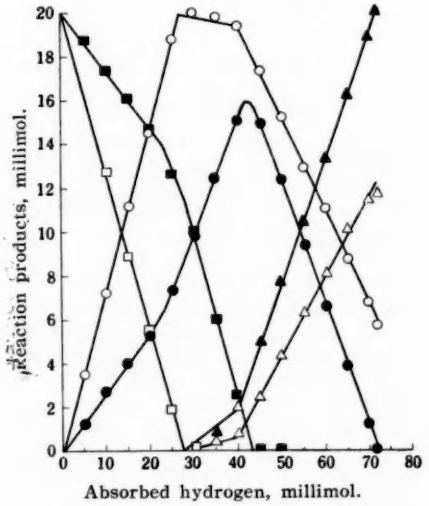

Fig. 7. The reaction products in the competitive hydrogenation of phenylacetylene and propargyl alcohol.
$Pd\text{-}CaCO_3$ catalyst 1.00 g.
Phenylacetylene (20 millimol.)
Propargyl alcohol (20 millimol.)
■ Phenylacetylene □ Propargyl alcohol
● Styrene ○ Allyl alcohol
▲ Ethylbenzene △ Propyl alcohol

the side reaction, and its hydrogenation was interrupted with the occurrence of the side reaction. The product from the side reaction was mainly propionaldehyde. However, it was found that propionaldehyde could not retard the hydrogenation of allyl alcohol, a mixture of methyl alcohol and propionaldehyde being used as a solvent.

Consideration

It is interesting to note that, when phenylacetylene has been absorbed on the catalyst surface, styrene is hydrogenated more easily than 1,4-butynediol, but, when the hydrogenation of phenylacetylene has been completed, 1,4-butynediol is hydrogenated more easily than styrene. Allyl alcohol is hydrogenated more easily than 1,4-butenediol. However, 1,4-butenediol is hydrogenated, even when the hydrogenation of allyl alcohol has been interrupted.

These results show that the catalyst properties are affeced by the adsorption of 1,4-butynediol, phenylacetylene, propargyl alcohol and so on. It is generally admitted that the catalyst properties are changed by the adsorbed substance[8]. When phenylacetylene or propargyl alcohol is adsorbed on the catalyst surface, the catalyst properties may be different from those when 1,4-butynediol is adsorbed. Accordingly, the partial hydrogenation of 1,4-butynediol might have been achieved on the Pd-$CaCO_3$ catalyst, with quinoline as a beneficial poison, but not phenylacetylene and propargyl alcohol.

It was shown that the gas chromatography is very useful to study the reactions.

The author is grateful to Professor T. Kusama, Yokohama National University, for his unfailing kindness in encouraging this work. The author is also indebted to Professor K. Tamaru, Yokohama National University, for his valuable advice, and Mr. Y. Suzuki, for his assistance.

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8) R. Suhrman and K. Schultz, *Z. physik. Chem.*, **1**, 69 (1954); W. H. Sachtler, *J. Chem. Phys.*, **35**, 751 (1956); L. E. Moore and P. W. Selwood, *J. Am. Chem. Soc.*, **78**, 697 (1956).

Dehydration of Bile Acids and their Derivatives. VII. Isomerization of Methyl 3α-Hydroxy-Δ⁷-cholenate to Methyl 3α-Hydroxy-Δ¹⁴-cholenate

By Ryuzaburo OSAWA and Kazumi YAMASAKI

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Yamasaki[1] reported previously that the action of concentrated hydrochloric acid on chenodeoxycholic acid gave three isomeric 3α-hydroxycholenic acids, but the localization of their double bonds has not yet been settled. In order to obtain any further information about these acids, the authors have attempted to isomerize 3α-hydroxy-Δ⁷-cholenic acid derived from chenodeoxycholic acid and to compare the product obtained with the isomers reported by Yamasaki[1]. Methyl 3α-ethoxycarbonyloxy-7α-hydroxycholanate (Ib) was prepared from methyl chenodeoxycholate (Ia) according to Fieser et al.[2] and dehydrated with phosphorus oxychloride in pyridine[3] to give methyl 3α-ethoxycarbonyloxy-Δ⁷-cholenate[4] in a fairly good yield, m.p. 136°C, $\alpha_D^{24}=+81.20°$ (Chf.) [Herz[5]: m.p. 126°C, $\alpha_D^{21}+80\pm2°$ (Di)].

Methyl 3α-hydroxy-Δ⁷-cholenate (IIc)

1) K. Yamasaki and K. Takahashi, *Z. physiol. Chem.*, **256**, 21 (1938); K. Yamasaki, *J. Chem. Soc. Japan, Pure Chm. Sec.* (*Nippon Kagaku Zasshi*), **72**, 680 (1951).

2) L. F. Fieser, J. E. Herz, M. W. Klohs, M. A. Romero and T. Utne, *J. Am. Chem. Soc.*, **74**, 3309 (1952).

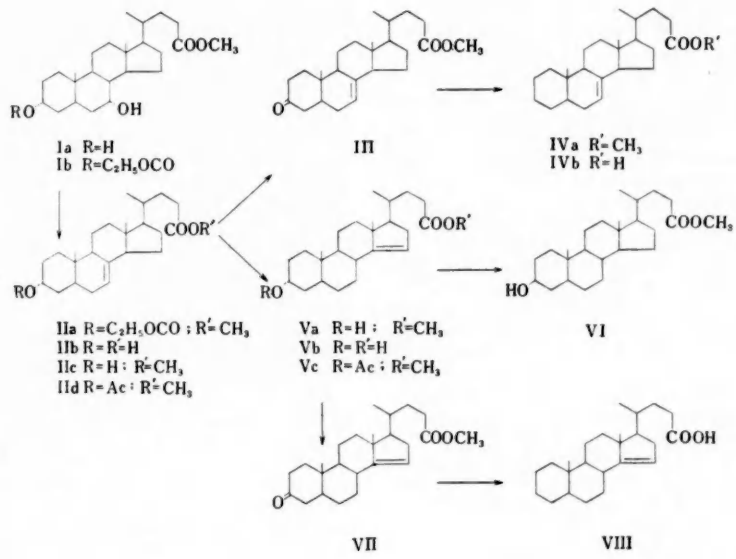
3) E. Berner, A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **30**, 1542 (1947).

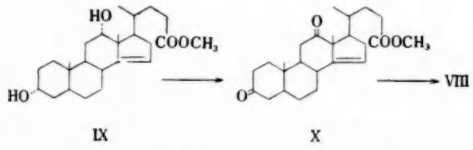
4) Although the proposed position (Δ⁷) of the double bond of this acid has not yet been studied, the position is highly probable, because the C_7 OH-group of chenodeoxycholic acid is apt to be dehydrated (*trans*-dehydration) exactly like cholic acid[3], and any possible shift of the double bond then formed can be excluded under the condition here described.

5) J. E. Herz, A thesis submitted to the Department of Chemistry, Harvard University (1951).

TABLE I. 3α-HYDROXYCHOLENIC ACIDS DERIVED FROM CHENODEOXYCHOLIC ACID

3α-Hydroxy-cholenic acid	m. p. °C	$[\alpha]_D$	Methyl ester, m. p., °C	Methyl ester acetate, m. p. °C
β-Apochenodeoxycholic acid[1]	195~196	+83.67° (alc.)	—	83~84
γ-Apochenodeoxycholic acid[1]	182~183	+101.73° (MeOH)	—	77~78
Chenocholenic acid[1]	211~213	+30.0° (MeOH)	—	—
3α-Hydroxy-Δ^7-cholenic acid	189~190	+62.0° (Di.)	108~109	127
3α-Hydroxy-Δ^{14}-cholenic acid	160	+62.8° (Chf.)	140~141	110





was subjected to isomerization by the action of dry hydrogen chloride gas[6], and a crystalline mixture was obtained. A fraction melting higher than the starting material was purified to afford crystals of m. p. 140~141°C, $\alpha_D^{20}=+55.8°$ (Chf.). The isomerized ester showed a distinct depression of the melting point on admixture with the starting substance and gave a negative selenium dioxide test, while the latter did a positive test, contrary to Fieser's report[7].

The corresponding free acid dissolved in ethanol showed an absorption maximum at 211 mμ with an extinction coefficient of ε_{max}^{EtOH} 2390, while $\Delta^{8(14)}$-cholenic acid as a reference substance, obtained from apocholic acid[8], showed an extinction coefficient of $\varepsilon_{max}^{EtOH}=6170$. According to Bladon et al.[9], this finding suggests that the new 3α-hydroxycholenate possesses either a tri- or a disubstituted ethylenic grouping. As was expected, the ester absorbed one mole of hydrogen on catalytic hydrogenation to give methyl lithocholate (VI) (m.p. 130°C). These results provide a strong evidence for the Δ^{14}-structure (V) of the new acid.

In order to ascertain the structure, the 3-hydroxy-ester (Va) was transformed into a cholenic acid by the Huang-Minlon reduction[10] of the corresponding 3-keto-ester (VII). The cholenic acid obtained was identified with Δ^{14}-cholenic acid (VIII) which was derived from 3α,12α-dihydroxy-Δ^{14}-cholenic acid[11] (IX) through its dehydro-acid (X).

6) K. Yamasaki, *Z. physiol. Chem.*, **233**, 10 (1935).
7) L. F. Fieser, *J. Am. Chem. Soc.*, **75**, 4395 (1953).
8) To be published.
9) P. Bladon, H. B. Henbest and G. W. Wood, *J. Chem. Soc.*, **1952**, 2737.
10) Huang-Minlon, *J. Am. Chem. Soc.*, **71**, 3301 (1949).
11) Cf. L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene", 3rd Ed., Reinhold Publishing Corp., New York (1949), p. 118.

Thus it is concluded that the isomerized product from methyl 3α-hydroxy-Δ^7-cholenate (IIc) is methyl 3α-hydroxy-Δ^{14}-cholenate (Va), but, as shown in Table I, the 3α-hydroxy-Δ^{14}-cholenic acid (Vb) was found to be different from any of the three 3α-hydroxycholenic acids obtained by Yamasaki[1]. The expected presence of the isomeric 3α-hydroxy-$\Delta^{8(14)}$-cholenate together with the Δ^{14}-ester in the isomerization product is now under investigation.

Experimental

Preparation of 3α-Hydroxy-Δ^7-cholenic Acid and Derivatives. — *Methyl 3α-ethoxycarbonyloxy-7α-hydroxycholanate (Ib).* — Two grams of methyl chenodeoxycholate (Ia) (the free acid, m.p. 140°C, was prepared according to Fieser and Rajagopalan[12] from cholic acid and the non-crystalline methyl ester was prepared with diazomethane as ususl) dissolved in 20 ml. of dioxane containing 3.2 ml. of pyridine was treated with 4 ml. of ethyl chloroformate with cooling in ice water. After standing at room temperature for 2 hr., the mixture was diluted with water, and extracted twice with ether. The combined extract was washed with dilute hydrochloric acid and with water, dried over sodium sulfate, and evaporated to dryness in vacuo. The residue was treated with a small quantity of methanol, warmed and allowed to stand at room temperature to crystallization. Recrystallization from methanol gave the ethoxycarbonyl derivative (Ib) in colorless blades, m. p. 136°C, $\alpha_D^{20} = +30.55°$ (Chf.).

Methyl 3α-ethoxycarbonyloxy-Δ^7-cholenate (IIa). — The above ester (Ib) (1.8 g.) was dissolved in 20 ml. of pyridine, 6 ml. of phosphorous oxychloride was added, and the mixture was kept at room temperature overnight. The reaction mixture was poured cautiously into 300 ml. of ice water, and extracted 3 times with ether. The combined ethereal extract was washed with water, dilute hydrochloric acid, aqueous sodium hydroxide solution and again water, successively, and dried over sodium sulfate. Removal of the solvent gave a crystalline residue, to which was added a small quantity of methanol, and the solution was warmed and allowed to stand at room temperature to give a crystalline product, m.p. 120~121°C. Yield, 1.65 g. Recrystallization from acetone gave the product in blades, m. p. 132~133°C, $\alpha_D^{24} = +81.2°$ (Chf.).

Anal. Found: C, 73.00; H, 9.63. Calcd. for $C_{28}H_{44}O_5$ (460.32): C, 73.01; H, 9.89%.

3α-Hydroxy-Δ^7-cholenic acid (IIb). — The above ester (IIa) (1.5 g.) was dissolved in 20 ml. of methanol containing 10 ml. of 10% aqueous potassium hydroxide and the solution was refluxed for 1.5 hr. The hydrolyzate was diluted with water and acidified with dilute hydrochloric acid. The precipitates were collected, washed with water and dried to give the free acid, m. p. 183~184°C. Yield, 1.17 g. Recrystallization from ethyl acetate and methanol gave the substance in needles, m. p. 189~190°C, $\alpha_D^{23} = +62.0°$ (Di). The selenium dioxide test was positive.

Anal. Found: C, 76.64; H, 10.05. Calcd. for $C_{24}H_{38}O_3$ (374.54): C, 76.94; H, 10.23%.

Methyl 3α-hydroxy-Δ^7-cholenate (IIc). — The above acid (IIb) (m. p. 190~191°C, 0.5 g.) was refluxed with 10 ml. of methanol containing two drops of concentrated hydrochloric acid for 1/2 hr., and the solution was concentrated by passing a stream of air to crystallization. After completion of crystallization, the crystals were collected and washed with a small volume of methanol, m. p. 104~105°C. Yield, 0.49 g.

Recrystallized twice from aqueous methanol, the substance was obtained in glistening leaflets, m. p. 108~109°C, $\alpha_D^{24} = +61.8 \pm 1.4°$ (Chf.).

Methyl 3α-acetoxy-Δ^7-cholenate (IId). — The above ester (IIc) (200 mg.) in 4 ml. of pyridine was treated with 2 ml. of acetic anhydride. After standing for 24 hr., water and concentrated hydrochloric acid (3.5 ml.) were added and the mixture was warmed for 20 min. on a steam bath. The solid was collected, and weighed 200 mg. Recrystallized once from methanol, the substance was obtained in glistening plates, m. p. 126~127°C, $\alpha_D^{23} = +86.0°$ (Chf.), λ_{max} 211 mμ, ε_{max}^{EtOH} 2075.

Anal. Found: C, 74.80; H, 9.64. Calcd. for $C_{27}H_{42}O_4$ (430.61): C, 75.30; H, 9.85%.

Methyl 3-keto-Δ^7-cholenate (III). — Methyl 3α-hydroxy-Δ^7-cholenate (IIc) (800 mg.) was oxidized in acetone with the chromic acid-H_2SO_4 mixture according to Baldon et al.[13] When the reaction was completed, the solution was diluted with water. After completion of crystallization in an ice box, the crystals were collected, m. p. 123~124°C. Yield, 770 mg. Recrystallized once, the substance was obtained in a pure state, m. p. 125°C, $\alpha_D^{23} = +53.3$ (Chf.).

Anal. Found: C, 77.22; H, 9.77. Calcd. for $C_{25}H_{38}O_3$ (386.55): C, 77.67; H, 9.91%.

Methyl Δ^7-cholenate (IVa). — Methyl 3-keto-Δ^7-cholenate (III) (0.51 g.) was heated with a mixture of triethylene glycol (30 ml.), hydrazine hydrate (1.5 ml.) and potassium hydroxide (1 g.) by the modified Wolff-Kishner method (Huang-Minlon[10] reduction).

The reaction mixture was diluted with water and acidified with dilute hydrochloric acid. The solid was collected, washed with water, and dried. The crude acid in methanol was treated with an ether solution of diazomethane and concentrated. The first crop (0.37 g.) showed m. p. 95.5~97°C, and the second (0.05 g.), m. p. 85~86°C.

Recrystallization of the combined crops from methanol-acetone gave thin rectangular plates of m. p. 98~99°C, undepressed by the sample obtained by the phosphorous oxychloride dehydration of methyl 7-hydroxycholanate (Herz[5]); $\alpha_D^{23} = +53 \pm 3°$ (Chf.) [$\alpha_D^{23} = +56 \pm 2°$ (Di.) (Herz[5])].

Anal. Found: C, 80.25; H, 10.58. Calcd. for $C_{23}H_{40}O_2$ (372.57): C, 80.62; H, 10.82%.

12) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **72**, 5530 (1950).

13) P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch and G. W. Wood, *J. Chem. Soc.*, **1951**, 2402.

Δ^7-Cholenic acid (IVb).—The above ester (IVa) (100 mg.) was refluxed for 1 hr. with 7 ml. of methanol and 3 ml. of 10% aqueous potassium hydroxide, and the reaction mixture was diluted with water and acidified with dilute hydrochloric acid. The crystalline solid was collected. Recrystallized twice from methanol, Δ^7-cholenic acid was obtained in a pure state, m. p. 150~151°C, undepressed on admixture with the specimen (m. p. 151°C) prepared by Herz[5]).

Anal. Found: C, 80.78; H, 10.47. Calcd. for $C_{24}H_{38}O_2$ (558.54): C, 80.80; H, 10.68%.

Isomerization of Methyl 3-Hydroxy-Δ^7-cholenate.—*Methyl 3α-hydroxy-Δ^{14}-cholenate (Va).*—A stream of dry hydrogen chloride gas was passed into a solution of methyl hydroxy-Δ^7-cholenate (IIc) (1.0 g.) in anhydrous chloroform (20 ml.) for 2 hr. at 0°C. The solution was diluted with chloroform with cooling in ice water, washed with water, soda solution and again with water, successively, and dried over sodium sulfate. Removal of the solvent gave a crystalline residue. This was dissolved in 1 ml. of benzene, passed throngh a Brockmann-alumina column and eluted with petroleum ether, benzene, ether and methanol, successively. The first portions of the elute contained the original substance, and a substance of higher melting point was obtained from the fractions eluted with ether. Rechromatography of the fractions of the higher melting point gave an ester of m. p. 139°C, and recrystallization from ethanol-water afforded crystals of m. p. 140~141°C, $\alpha_D^{20}=+55.8°$ (Chf.), which showed a depression in the melting point on admixture with the starting substance and was negative in the selenium dioxide test.

Anal. Found: C, 77.40; H, 10.13. Calcd. for $C_{25}H_{40}O_3$ (388.32): C, 77.69; H, 9.91%.

Methyl 3α-acetoxy-Δ^{14}-cholenate (Vc).—Methyl 3α-hydroxy-Δ^{14}-cholenate (Va) (m. p. 141°C, 100 mg.) in 2 ml. of pyridine was treated with 1 ml. of acetic anhydride. After standing for 24 hr., water and concentrated hydrochloric acid (3.5 ml.) were added to the reaction mixture, and the whole was warmed for 20 min. on a steam bath. The solid was collected. Yield, 100 mg. Recrystallized once from methanol, the product was obtained in glistening leaflets of m. p. 110°C, $\alpha_D^{20}=+86.7°$ (Chf.).

Anal. Found: C, 75.30; H, 9.85. Calcd. for $C_{27}H_{42}O_4$ (430.61): C, 75.30; H, 9.85%.

3α-Hydroxy-Δ^{14}-cholenic acid (Vb).—Methyl 3α-hydroxy-Δ^{14}-cholenate (Va) (100 mg.) was dissolved in 7 ml. of methanol containing 3 ml. of 10% aqueous potassium hydroxide and the mixture was refluxed for 1 hr. The solution was acidified with dilute hydrochloric acid. The crystalline solid was collected. Recrystallized twice from methanol containing ethyl acetate, the substance was obtained in a pure state, m. p. 161°C, $\alpha_D^{24}=+62.8°$ (Chf.), λ_{max} 211 mμ, ε_{max}^{EtOH} 2390.

Anal. Found: C, 76.27; H, 10.37. Calcd. for $C_{24}H_{38}O_3$ (374.54): C, 76.94; H, 10.23%.

Methyl lithocholate (VI).—Methyl 3α-hydroxy-Δ^{14}-cholenate (Va) (m. p. 141°C, 50 mg.) in 10 ml. of glacial acetic acid was shaken for 3 hr. with 10 mg. of PtO_2 (Adams) and hydrogen, 3.1 ml. of hydrogen being absorbed (the calculated amount: 3.07 ml.). Concentration of the solution, addition of a small amount of methanol and heating gave needles. Recrystallization from methanol afforded a sample of m. p. 130°C, $\alpha_D^{20}=+24.2°$ (Chf.). This showed no depression in the melting point on admixture with authentic methyl lithocholate (m. p. 129~130°C).

Anal. Found: C, 77.48; H, 10.17. Calcd. for $C_{25}H_{42}O_2$ (375.58): C, 76.78; H, 10.83%.

Methyl 3-keto-Δ^{14}-cholenate (VII).—Methyl 3α-hydroxy-Δ^{14}-cholenate (Va) (m. p. 141°C, 200 mg.) in 20 ml. of acetone was oxidized with the chromic acid-H_2SO_4 mixture according to Bladon et al.[13]) After completion of oxidation, the excess of the oxidant was destroyed by addition of a small quantity of methanol. The solution was diluted with water and extracted with ether. The ether extract was washed with water, soda solution and again with water, successively, dried over sodium sulfate and evaporated. The residue was triturated with a small quantity of methanol, and kept at room temperature. The yield of colorless needles, m. p. 78~79°C, was 155 mg. Recrystallized twice from aqueous methanol, the substance was obtained in a pure state, m. p. 89~90°C, $\alpha_D^{24}=+38.8°$ (Chf.).

Anal. Found: C, 77.40; H, 10.13. Calcd. for $C_{25}H_{38}O_3$ (386.55); C, 77.69, H. 9.09%.

Δ^{14}-Cholenic acid (VIII).—Reduction of methyl 3-keto-Δ^{14}-cholenate (VII) (100 mg.) was conducted according to the modified Huang-Minlon procedure[10]) with a mixture of triethylene glycol (10 ml.), hydrazine (1 ml.) and potassium hydroxide (1 g.). The reaction mixture was diluted with water and acidified with dilute hydrochloric acid. The solid was collected, washed with water, dried over sodium sulfate, and evaporated. Recrystallization from ethyl acetate and then from aqueous methanol afforded colorless needles of m. p. 143~144°C, $\alpha_D^{22}=+61.8°$ (Chf.), ε_{max}^{EtOH} 3404.

Anal. Found: C, 80.44, H, 10.71. Calcd. for $C_{24}H_{38}O_2$ (358.54): C, 80.39; H, 10.68%.

Derivation of Δ^{14}-cholenic Acid from 3,12-Dihydroxy-Δ^{14}-cholenic Acid.—*Methyl 3,12-diketo-Δ^{14}-cholenate (X).*—Methyl 3,12-dihydroxy-Δ^{14}-cholenate (IX) (200 mg.) was oxidized with the chromic acid-H_2SO_4 mixture according to Bladon et al.[13]) Recrystallization from methanol gave fine needles of m. p. 134°C, $\alpha_D^{22}=+60.3$ (Chf.). Yield, 0.175 g.

Anal. Found: C, 75.18; H, 9.15. Calcd. for $C_{25}H_{36}O_4$ (400.56): C, 74.96; H, 9.06%.

Δ^{14}-Cholenic acid (VIII).—The above diketoester (X) (200 mg.) was reduced by the Huang-Minlon procedure[10]) (25 ml. of triethylene glycol, 2 ml. of hydrazine hydrate, 2 g. of potassium hydroxide). Recrystallization from acetone and then acetic acid gave crystals of m.p. 142~143°C, $\alpha_D^{20}=+62.1°$ (Chf.). This acid showed no depression of the melting point on admixture with the specimen obtained above from 3α-hydroxy-Δ^{14}-cholenic acid.

Anal. Found: C, 79.59; H, 10.75. Calcd. for $C_{24}H_{38}O_2$ (358.54): C, 80.39; H, 10.68%.

The preparation of methyl Δ^7-cholenate from methyl 3α-hydroxy-Δ^7-cholenate was carried out, when Yamasaki was working in L. F. Fieser's Laboratory, Harvard University. The elementary analyses were carried out by Mr. Okada of the Analysis Room of Shionogi Laboratory, to whom the authors' gratitude is due.

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The Silver Catalyzed Oxidation of Arsenious Acid by Persulfate

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The uncatalyzed oxidation of arsenious acid by persulfate has been studied by Gupta & Ghosh[1] and Gupta[2] has found the specific influence of several ions in this oxidation. The oxidation is similar to other uncatalyzed oxidations such as those of thiosulfate[3] and oxalate[4,5] ions. Catalysis by silver ion has been reported by Gupta and Ghosh, but no systematic study was made by them. Silver catalyzed oxidations by persulfate are reported to be of three types. Hence a detailed study of this silver catalyzed reaction was made to evaluate a possible mechanism and to compare the results with those of other silver catalyzed oxidations.

Experimental

Persulfate oxidations are very susceptible to impurities of the solutions and the nature of the glass vessel, and hence all the vessels and apparatus used in this investigation, were of Jena glass. The medium of reaction was redistilled water.

All the chemicals used were of B.D.H.A.R. or E. Merck G.R. quality. A stock solution of 0.20 N arsenious acid was prepared. For this, a requisite amount of arsenious oxide, sufficient to give a little more than 0.20 N acid, was dissolved by boiling in redistilled water. After allowing it to cool, it was filtered and standardized against permanganate solution. Persulfate solution was always freshly prepared and its concentration checked by Eckardt's method[6]. All other solutions were prepared in the usual way.

The reaction was studied at 24°C in a thermostat and silver nitrate was added at the end. A preliminary study indicated that there was practically no reaction between persulfate and arsenious acid at 24°C for about 30~40 min., the time for which they were kept together in the reaction vessel. The reaction speed becomes measurable only at higher temperatures. Gupta and Ghosh studied the uncatalyzed reaction at 45°C.

Five milliliters of the reaction mixture were pipetted out at suitable intervals of time, in a beaker containing 3 ml. of pure and concentrated hydrochloric acid and 10~15 ml. of distilled water. One drop of 0.0025 M KIO_3 added and the contents were titrated against 0.01 N $KMnO_4$ from a microburette. Persulfate did not interfere with this titration. The reaction was completely checked by inhibiting chloride ions[2].

Results and Discussion

The oxidation is of the first order in persulfate and the constants have been calculated from the relation,

$$k = (2.303/t) \times (1/C_{Ag^+}) \times \log [a/(a-x)]$$

where 'a' and '$a-x$' are the concentrations of the persulfate initially and after time 't', respectively, and C_{Ag^+} is the concentration of the silver ions. The reaction is in fact bimolecular, but has a first order rate constant because the concentration of the catalyst Ag^+ does not change during the course of the reaction. Hence k, though a first order constant, has the units of l. equi^{-1} min^{-1}.

1) Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, **11**, 62 (1959).
2) Y. K. Gupta, *J. Ind. Chem. Soc.*, **36**, No. 9 (1959).
3) C. V. King and O. F. Steinbach, *J. Am. Chem. Soc.*, **52**, 4779 (1930).
4) C. V. King, ibid., **50**, 2089 (1928).
5) T. L. Allen, ibid., **73**, 3589 (1951).
6) Le Blank Eckardt, *Chem. News*, **81**, 38 (1900).

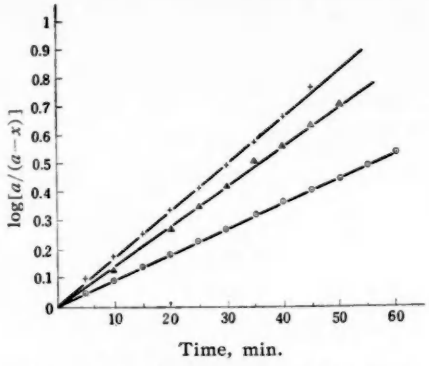

Fig. 1. Silver catalyzed oxidation of H_3AsO_3 by $K_2S_2O_8$.
⊙ Sample 1; k=23.96
△ Sample 2; k=31.49
× Sample 3; k=36.77

Gupta and Ghosh[1] obtained different results with different samples of arsenious acid solution. It was, therefore, imperative to study also the catalyzed reaction with different samples of acid solution. Three experiments out of 20 are shown in Fig. 1 where the average k varied within appreciable limits.

However, the results are quite reproducible with the same sample of arsenious acid solution and hence in order to compare the results amongst themselves, it was necessary to use the same stock solution of arsenious acid as was done by Gupta and Ghosh. Efforts were made to eradicate the cause of this trouble, but without any success. The present paper reports the results of experiments using sample 1 of Fig. 1. The reaction is specifically influenced by the ions and hence no electrolyte was added to keep the ionic strength constant. Nor was there any need for it, because in any particular experiment no change in k was observed as the reaction progressed.

Table I shows the results using different concentrations of the reactants.

It may be seen that the reaction is independent of the concentration of arsenious acid—a fact found in other persulfate oxidations where it is independent of the concentration of the reductant. The rate of reaction increases with the increase in the concentration of the persulfate, but the constants decrease, probably due to the inhibition by potassium ions. The inhibiting character of the potassium ions have been reported in the oxidation of formate[7], oxalic acid[8] and oxalate[9], and the decomposition of persulfate[10]. Alkali metal ions, in general, inhibit many persulfate oxidations.

TABLE I

$K_2S_2O_8$, N	H_3AsO_3, N	k
0.005	0.0102	25.80
0.01	0.0102	23.96
0.02	0.0102	19.80
0.04	0.0102	13.82
0.01	0.0051	24.01
0.01	0.0102	23.96
0.01	0.0204	24.59

Specific Effect of the Ions.—Table II gives the average values of k for the kinetics of this reaction in the presence of several electrolytes.

TABLE II

$K_2S_2O_8$=0.01 N; H_3AsO_3=0.0102 N; $AgNO_3$=0.001 M

Electrolyte	Concn., M	k
—	—	23.96
K_2SO_4	0.25	7.49
K_2SO_4	0.125	8.49
$(NH_4)_2SO_4$	0.25	11.22
$(NH_4)_2SO_4$	0.125	11.71
$MgSO_4$	0.25	7.93
$MgSO_4$	0.125	9.88
KNO_3	0.50	10.72
KNO_3	0.25	11.44
$NaNO_3$	0.25	16.50
$NaNO_3$	0.125	18.96
NH_4NO_3	0.50	13.80
NH_4NO_3	0.25	18.21

There is no regular variation in k with the change in the ionic strength of the reaction mixture and hence no conclusion regarding the salt effect could be obtained. A comparison of the results shows that the inhibiting action is in the order $K^+ > Na^+ > NH_4^+$——a conclusion similar to that of uncatalyzed oxidation[2]. When the results for nitrates and sulfates are compared, it may be seen that either sulfate ion inhibits or the nitrate ion accelerates. However, the possibilty of both is also considered. In any reaction a sulfate ion is gradually produced, but no increase or decrease in the constants was observed as the reaction progressed. Hence the sulfate ion seems to have no effect or little effect in this reaction and the reaction rate is higher in presence of nitrates than

7) S. P. Srivastava and S. Ghosh, *Z. physik. Chem.*, **202**, 198 (1953).
8) S. P. Srivastava and S. Ghosh, ibid., **205**, 332 (1956).
9) Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, accepted (1959).
10) A. Kailan and L. Olbrich, *Monatshe. Chem.*, **47**, 449 (1927).

of sulfates, due to the acceleration by nitrate ions.

Reaction in Presence of CH_3COONa, CH_3COONH_4 and CH_3COOH.—Five concentrations of CH_3COONa were investigated and it was found that there exists an optimum concentration of sodium acetate for which the reaction is fastest. Fig. 2 shows the average constants for different concentrations of sodium acetate.

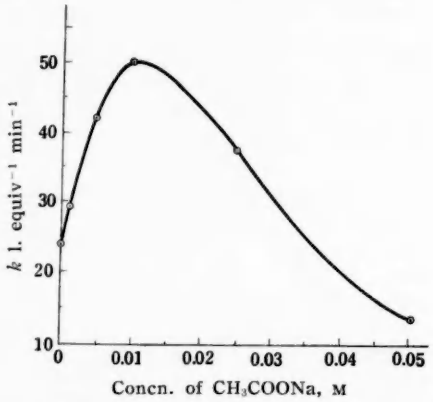

Fig. 2. Effect of CH_3COONa in the silver catalyzed oxidation of H_3AsO_3 by $K_2S_2O_8$.

The sodium ion has been found to inhibit and hence the acetate ion must catalyze the reaction. It appears that at lower concentrations of CH_3COONa, the catalyzing influence of acetate ions predominates over the inhibiting action of sodium ions; whereas the reverse is true at higher concentrations of sodium acetate. The accelerating action of acetate ions may further be seen in Table III where the results with acetic acid and ammonium acetate are shown.

TABLE III

$K_2S_2O_8 = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Electrolyte	Concn., M	k
CH_3COOH	0.40	40.27
CH_3COOH	0.10	39.70
CH_3COONH_4	0.50	4.94
CH_3COONH_4	0.25	6.16

Higher concentrations of sodium acetate could not be employed because a precipitate of possibly sodium arsenite formed. This, however, disappeared as the reaction progressed. Results with ammonium acetate are quite as expected.

Reaction in Presence of Sulfuric Acid.—Seven

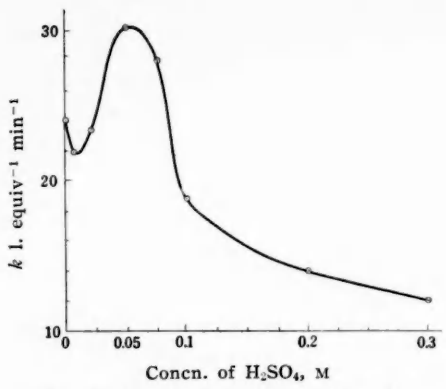

Fig. 3. Effect of H_2SO_4 in the silver catalyzed oxidation of H_3AsO_3 by $K_2S_2O_8$.

concentrations of sulfuric acid were employed and the results are graphically shown in Fig. 3.

There is a concentration of sulfuric acid for which the reaction is fastest. The rate decreases below or above that concentration. The rate constant is 30.26 l. equi^{-1} min^{-1} at this concentration. It may appear from Fig. 3 that hydrogen ions inhibit and sulfate ions slightly accelerate, although the latter have been found to be without any effect. The actual mechanism is not clear. In fact, it is difficult to explain the behavior of sulfuric acid in persulfate oxidations. In the silver catalyzed oxidations of oxalic acid[11] and hydrogen peroxide[12], sulfuric acid retards the rate, whereas it accelerates the rate in the uncatalyzed oxidation of oxalic acid[8] and silver catalyzed oxidation of potassium oxalate[9].

Action of Nitrate, Aluminum and Manganous Ions.—When nitric acid is used, the reaction is very slow in the initial stages, but the rate increases quickly with time. The average constants as shown in Table IV, are found to increase till the end of the reaction.

It seems that there is some impurity in nitric acid which helds up the reaction in the beginning. Further on comparing these results with those in the presence of sulfuric acid, it is evident that the rate is higher in the presence of nitric acid. Hence nitrate ions accelerate the rate.

The results with aluminum nitrate and

11) Y. K. Gupta and S. Ghosh, *Proc. Nat. Acad. Sci., India*, **27A Part V**, 258 (1958).
12) S. P. Srivastava and S. Ghosh, ibid., **23A Part VI**, 44 (1954).

TABLE IV

$K_2S_2O = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Time min.	0.016 M HNO_3		0.16 M HNO_3	
	$KMnO_4$ ml.	k	$KMnO_4$ ml.	k
0	5.10	—	5.10	—
5	4.96	1.61	—	—
10	4.28	15.57	—	—
15	3.66	20.80	—	—
20	3.16	22.95	4.92	0.86
25	2.68	24.91	4.52	4.04
30	2.24	26.76	4.04	7.10
35	1.90	27.64	3.62	9.51
40	1.58	28.82	3.20	11.16
45	1.38	28.60	—	—
50	1.18	28.88	2.56	13.38
55	0.98	29.63	2.28	14.28
60	—	—	2.00	15.33

TABLE V

$K_2S_2O_8 = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Electrolyte	Concn., M	k
$Al(NO_3)_3$	0.0625	80.60
$Al(NO_3)_3$	0.01	80.01
$Al_2(SO_4)_3$	0.0625	28.66
$Al_2(SO_4)_3$	0.01	25.93
$MnSO_4$	0.002	7.32
$MnSO_4$	0.001	11.45

aluminum sulfate are shown in Table V. The reaction is very fast in the presence of aluminum nitrate. The rate only slightly increases in the presence of aluminum sulfate.

From this it appears that nitrate ions greatly catalyze the reaction and sulfate does so only slightly, whereas aluminum is without any effect. It may, however, be mentioned that the rate constants gradually decreased in the case of aluminum nitrate and increased in the case of aluminum sulfate till the end of the reaction, and that the above table gives only the average constants. The increase or decrease was 15 to 20%.

Manganous sulfate was used because it has been found to act as a catalyst or an anticatalyst in many of the persulfate oxidations. The authors believe that Mn(II) has a specific inhibiting effect.

Energy and Entropy of Activation.—The energy of activation has been calculated from the results of experiments at three different temperatures. Table VI gives the constants at these temperatures.

The average energy of activation was 8941 cal. The frequency factor[13] and the

13) Calculated from the relation $k = A \times e^{-E/RT}$ where A is the frequency factor.

TABLE VI

$K_2S_2O_8 = 0.01$ N; $H_3AsO_3 = 0.0102$ N; $AgNO_3 = 0.001$ M

Temp. °C	k
24	23.96
29	30.54
39	50.00

entropy[14] calculated from this, are 1.55×10^6 l. equiv^{-1} sec^{-1} and -31.06 E.U., respectively. These values correspond to the overall reaction and they may be quite different for the rate determining step. Also these values may vary from sample to sample of arsenious acid, but their nature and order of magnitude do help us to arrive at a possible mechanism.

The rate is the first order in persulfate and independent of the concentration of arsenious acid. No conclusion regarding the salt effect could be obtained. The authors propose the following mechanism for the silver catalyzed oxidation of arsenious acid by persulfate.

$$S_2O_8^{2-} \rightleftarrows 2SO_4^- \quad \text{rapid (1)}$$

$$2SO_4^- + Ag^+ \rightarrow 2SO_4^{2-} + Ag^{3+} \quad \text{slow (2)}$$

$$Ag^{3+} + 2H_2O \rightarrow Ag^+ + 2H^+ + 2OH \quad \text{fast (3)}$$

$$H_3AsO_3 + 2OH \rightarrow H_3AsO_3 + H_2O \quad \text{fast (4)}$$

The existence of free radicals[15] SO_4^- and OH, and higher valent silver, Ag^{3+} is now beyond doubt. Gupta and Ghosh[16] have discussed the possibilty of higher valent silver in a paper on the silver catalyzed oxidation of Mn(II) by persulfate. The rate determining step 2 is preceded by an equilibrium which has a very small equilibrium constant K, of the order of 10^{-8} or even less. Step 2 is really bimolecular or rather termolecular, but has a first order dependence on the concentration of the persulfate as shown below.

$$-dc/dt = k_2[Ag^+][SO_4^-]^2$$

but $K[S_2O_8^{2-}] = [SO_4^-]^2$ from reaction 1.

Hence $-dc/dt = k_2K[S_2O_8^{2-}][Ag^+]$

$= k_r[S_2O_8^{2-}]$ where $k_r = k_2K[Ag^+]$

The silver ion concentration remains constant and hence the slow step is the first order in persulfate. Experimentally determined k is equal to $k_r/[Ag^+]$. Hence

14) Calculated from the relation $k = (KT/h) \cdot e^{\Delta S/R} \cdot e^{-\Delta H/RT}$ where ΔS the entropy change and ΔH is not much different than E.

15) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

16) Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, **9**, 178 (1959).

$k=k_2K$ or $k_2=k/K=23.96/10^{-8}$ or 23.96×10^8 l. equiv^{-1} min^{-1}. Based on this value of k_2, the entropy change for the slow step is +5.47 E.U. Absolute entropy values have no meaning. Reactions are faster or slower according as their entropy changes are positive or negative as compared to standard values. A standard value for comparision for bimolecular reactions is about −12 E.U. (calculated for the frequency factor, 10^{11}). There is an entropy increase[17] if the reactants are oppositely charged ions and hence the slow step 2 is supported by a positive entropy change. The generally accepted mechanism is, $S_2O_8^{2-}+Ag^+=2SO_4^{2-}+Ag^{3+}$. If this were the rate determining step, entropy change for the overall reaction should directly support this. The overall entropy change is negative and hence the authors disapprove the slow step between $S_2O_8^{2-}$ and Ag^+. With a prior equilibrium, the entropy change for the slow step 2 is positive and hence step 2 must be preferably between oppositely charged ions, i. e. the reaction is between positively charged silver ion and a negative ion from persulfate, but not persulfate itself.

Gupta and Ghosh[1] have proposed two mechanisms for the uncatalyzed oxidation of arsenious acid by persulfate.

$$S_2O_8^{2-} \rightleftarrows SO_4+SO_4^{2-} \quad \text{slow}$$

or $$S_2O_8^{2-}+2H_2O \rightleftarrows 2HSO_4^-+2OH \quad \text{slow}$$

Since the silver catalyzed oxidation of arsenious acid is very similar to the uncatalyzed oxidation, particularly in so far as the specific effect of the ions is concerned, it is reasonable to conclude that reaction mechanisms must also be similar. Hence it is believed that OH is preferably the radical responsible for oxidation in the uncatalyzed reaction.

This silver catalyzed oxidation is comparable to the fast oxidation of oxalate[9], and is much faster than the other type of catalyzed reactions wherein the specific rate constant lies between 0.2 and 0.3 at 25°C. Such oxidations are those of Cr(III)[18], VO(II)[19], Mn(II)[20], Ce(II)[21] and many other ions.

Summary

The kinetics of silver catalyzed oxidation of arsenious acid has been followed by estimating the acid with the permanganate. The results are reproducible only with the same stock solution of arsenious acid. This oxidation is much faster than other silver catalyzed oxidations, such as those of Cr^{3+}, VO^{2+}, Mn^{2+}, Ce^{2+}, etc. The oxidation is of the first order in persulfate and independent of the concentration of the acid. The entropy of activation has been calculated and a mechanism has been suggested. No conclusion regarding the salt effect could be obtained due to the specific effect of the ions. K^+, Na^+, NH_4^+ and Mg^{2+} inhibit in the order given. Nitrate ion accelerates the rate and sulfate ion seems to have no effect.

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17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley & Sons, Inc., New York (1953), p. 132.

18) D. M. Yost, *J. Am. Chem. Soc.*, **48**, 152 (1926).
19) D. M. Yost and W. Claussen, ibid., **53**, 3349 (1931).
20) A. O. Dekker, H. A. Levy and D. M. Yost, ibid., **59**, 2129 (1937).
21) W. H. Cone., ibid., **67**, 78 (1945).

Zur Darstellung von Polymethoxy-o-phthalaldehydsäuren

Von Eturô MAEKAWA und Seiko NAN'YA

(Eingegangen am 18. Mai 1959)

Polymethoxyphthalaldehydsäuren sind von Bedeutung, weil sie durch Grignardreaktion mit Methylmagnesiumjodid 3-Methylphthalide geben, die als Ausgangsprodukte zur Darstellung von Seeigelfarbstoffen interessant sind[1]. Edwards, Perkin und Stoyle[2] oxydierten Mekonin mit Braunstein in verdünnter Schwefelsäure zur Opiansäure. Es ist aber schwierig, die Oxydation genau zu kontrollieren. Stevens und Robertson[3] versuchten, 5.6-Methylendioxyphthalid mit Bleidioxyd oder Chromsäure zu 4.5-Methylendioxyphthalaldehydsäure zu oxydieren, konnten jedoch keine günstigen Ergebnisse bekommen. Da der Phthalidring im alkalischen Medium geöffnet wird, kann man die Oxydation besser alkalisch durchführen. Obgleich in den stark alkalischen Lösungen die durch Oxydation zuerst entstandene Phthalaldehydsäure sogar die Neigung zeigt[4], durch Cannizarosche Reaktion zu Phthalsäure und Phthalalkoholsäure, nämlich dem Ausgangsprodukt, zu disproportionieren, scheinen die Phthalide in schwach alkalischen Medien leicht zu Phthalaldehydsäuren oxydiert zu werden. Blair, Brown und Newbold[5] erhielten z. B. aus Mekonin bzw. 5.6.7-Trimethoxyphthalid (XIII) und Dimethylamin in Alkohol bei Raumtemperatur 2-Hydroxymethyl-5.6-dimethoxy- bzw. 2-Hydroxymethyl-4.5.6-trimethoxybenzoesäuredimethylamid, das durch Chromsäureoxydation in Eisessig in der Kälte und durch anschließende Verseifung mit verdünnter Salzsäure Opiansäure bzw. 4.5.6-Trimethoxyphthalaldehydsäure (XIV) in etwa 40%-iger Ausbeute ergab. Andererseits wird aus 3-Bromphthalid durch Hydrolyse mit Wasser *o*-Phthalaldehydsäure leicht hergestellt[6], welcher man aus Phthalid durch direktes Bromieren bei erhöhter Temperatur[6] oder durch Versetzen mit *N*-Bromsuccinimid (abgekürzt NBS) nach Hirshberg, Lavie und Bergmann[7] in guten Ausbeuten erhalten kann. Zur Darstellung der Polymethoxyphthalaldehydsäuren scheint sich das direkte bromieren schlechter zu eignen als das Verfahren mit NBS, weil die Gefahr darin besteht, daß der, während der Reaktion der Phthalide mit Brom entwickelte Bromwasserstoff bei der Reaktionstemperatur, nämlich bei 130~150°C, die Methoxygruppe abspaltet. Brown und Newbold[8] erhielten durch die Methode mit NBS *m*-Opiansäure und 4.5-Methylendioxyphthalaldehydsäure aus den entsprechenden Phthaliden in guten Ausbeuten, erwähnten jedoch, daß diese Reaktion auf die Phthalide, die, wie Mekonin, am Benzolkern leicht substituierbare Stelle besitzen, im allgemeinen nicht anwendbar ist[5]. Nach der in der Literatur beschriebenen Vorschrift[7,8] mit etwa doppelter molekularer Menge an NBS konnte in der früheren Arbeit[1] aus 4.5.6-Trimethoxyphthalid (I) keine erwartete Aldehydsäure (II) erhalten werden, wobei die Reaktion aber nicht weiter probiert wurde. Unter Verwendung von äquimolekularer Menge an NBS wird jedoch 3.4.5.6-Tetramethoxyphthalaldehydsäure (V) aus 4.5.6.7-Tetramethoxyphthalid (IV) in 85%-iger Ausbeute hergestellt[1]. Um optimale Bedingungen zur Darstellung der Polymethoxyphthalaldehydsäuren aus den entsprechenden Phthaliden zu finden, wird deren Reaktion mit NBS weiter untersucht.

IV ergibt durch Behandeln mit doppelter molekularer Menge an NBS und durch anschließende Hydrolyse des Produktes mit Wasser in nah-quantitativer Ausbeute 3.4.5.6-Tetramethoxyphthalsäure(VI), deren Konstitution durch Elementaranalyse sowie durch die Bildung des Anhydrids beim Erhitzen und durch IR-Absorptionsspektrum* festgestellt wurde.

1) F. Weygand, H. Weber und E. Maekawa, *Chem. Ber.*, **90**, 1879, (1957).
2) G. A. Edwards, W. H. Perkin und F. W. Stoyle, *J. Chem. Soc.*, **127**, 195 (1925).
3) T. S. Stevens und M. C. Robertson, ebenda, **1927**, 2790.
4) G. H. Beckett und C. R. A. Wright, ebenda, **29**, 281 (1876).
5) J. Blair, J. J. Brown und G. T. Newbold, ebenda, **1955**, 708.
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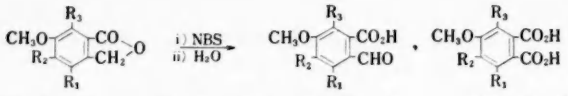
8) I. J. Brown und G. T. Newbold, ebenda, **1952**, 4397.

* Für die Aufnahme der IR-Spektren danken wir Herrn Prof. Dr. Y. Ishii (Organ.-Chem. Inst. der Techn. Fak. der Univ. Nagoya) bestens.



I: $R_1=R_2=OCH_3$, $R_3=H$ II: $R_1=R_2=OCH_3$, $R_3=H$ III: $R_1=R_2=OCH_3$, $R_3=H$
IV: $R_1=R_2=R_3=OCH_3$ V: $R_1=R_2=R_3=OCH_3$ VI: $R_1=R_2=R_3=OCH_3$
VII: $R_1=R_2=H$, $R_3=OCH_3$ VIII: $R_1=R_2=H$, $R_3=OCH_3$ IX: $R_1=R_2=H$, $R_3=OCH_3$
X: $R_1=R_3=H$, $R_2=OCH_3$ XI: $R_1=R_3=H$, $R_2=OCH_3$ XII: $R_1=R_3=H$, $R_2=OCH_3$
XIII: $R_1=H$, $R_2=R_3=OCH_3$ XIV: $R_1=H$, $R_2=R_2=OCH_3$
XV: $R_1=R_2=OCH_3$, $R_3=CH_3$ XVI: $R_1=R_2=OCH_3$, $R_3=CH_3$

Aus I konnte durch Behandeln mit äquimolekularer Menge an NBS und durch anschließende Hydrolyse 3.4.5-Trimethoxyphthalaldehydsäure (II) in einer Ausbeute von 77% hergestellt werden. Unter Verwendung von doppelter molekularer Menge an NBS bildete sich nach der Hydrolyse als Hauptprodukt 3.4.5-Trimethoxyphthalsäure (III) und daneben auch eine kleine Menge II. Die auf diese Weise hergestellte Aldehydsäure II fällt aus Wasser zum größten Teil als Nadeln aus, die bei 129°C schmelzen, und aus Äthanol oder Chloroform zum größten Teil als Nadeln, die bei 135°C schmelzen. Beide Kristalle unterscheiden sich durch ihr Aussehen sowie durch die Geschwindigkeit der Auflösung in verschiedenen Lösungsmitteln, wobei der höherschmelzende Kristall sich im allgemeinen langsamer löst, ergeben jedoch identisches 2.4-Dinitrophenylhydrazon. Phthalaldehydsäuren können bekanntlich nicht nur als Aldehydsäuren sondern unter Umständen auch als 3-Oxyphthalide reagieren. Opiansäure reagiert z. B. sowohl mit den Aldehydreagenzien als auch mit Alkoholen unter Bildung von 3-Alkoxymekoninen[9,10], die in die normalen Ester der Opiansäure übergehen können. Buu-Hoï stellte fest[11], daß *o*-Phthalaldehydsäure und ihre kernsubstituierten Derivate nach UV-Spektren in Wasser fast ausschließlich als echte Aldehydsäure, in Chloroform zum größten Teil als 3-Oxyphthalid und in Alkoholen als ein Gleichgewichtsgemisch aus beiden Isomeren existieren. Die IR-Spektren der beiden Kristallarten von II in KBr (Abb. 1 u. 2) unterscheiden sich durch Absorptionen bei 1700~1800 cm^{-1}, sind beide jedoch sehr ähnlich dem der *o*-Phthalaldehydsäure in KBr[12], während das IR-Spektrum der Chloroformlösung von II (Abb. 3) eine dem Phthalidring typische Bande bei 1768 cm^{-1} zeigt und keine Bande, die der echten Phthalaldehydsäure zuzuordnen ist. Daher wird angenommen, daß der Unterschied zwischen beiden Kristallarten von der Säure II, die im kristallinischen Zustand als echte Phthalaldehydsäure existiert, auf den der Kristallstruktur zurückzuführen ist, obgleich, wie unten erwähnt, der niedrigerschmelzende Kristall nicht fähig ist, durch Grignardreaktion mit Methylmagnesiumjodid 3-Methyl-4.5.6-trimethoxyphthalid zu ergeben.

Die oben beschriebenen Polymethoxyphthalsäuren, nämlich III und VI, reagieren mit 2.4-Dinitrophenylhydrazin viel schneller als Phthalsäure selbst unter Bildung der 2.4-Dinitrophenylhydrazone ihrer Anhydride.

Gegen die Meinung von Blair u. a.[5] ergibt Mekonin (VII) Opiansäure in relativ guter Ausbeute unter Verwendung von äquimolekularer Menge an NBS und 3.4-Dimethoxyphthalsäure (IX) mit doppelter Menge an NBS. Zur Darstellung von *m*-Opiansäure (XI) aus X ist auch unsere Vorschrift mit äquimolekularer Menge an NBS besser geeignet als die von Brown u. a.[8] mit überschüssigem NBS, nach welcher sich beim Nachprüfen in unserem Laboratorium *m*-Hemipinsäure in erheblicher Menge ergab. Auch der aus *m*-Mekonin nach McRae u. a.[13] hergestellte 5.6.7-Trimethoxyphthalid (XIII) gibt 4.5.6-Trimethoxyphthalaldehydsäure (XIV) bzw. 3.4.5-Trimethoxyphthalsäure (III) je nach der Menge an verwendetem NBS. 4.5.6-Trimethoxy-7-chlormethylphthalid, der aus Gallussäuretrimethyläther nach King und King[14] hergestellt wurde, ergibt durch Reduktion mit Zinkstaub und Essigsäure 4.5.6-Trimethoxy-7-methylphthalid (XV), der durch Versetzen mit äquimolekularer Menge an NBS 3.4.5-Trimethoxy-6-methylphthalaldehydsäure (XVI) ergab. XVI kristallisierte wieder in zwei verschiedenen

9) A. Kirpal, *Ber. dtsch. chem. Ges.*, **60**, 382 (1927).
10) W. M. Radionowa und A. M. Fedorowa, ebenda, **59**, 2949 (1926).
11) Buu-Hoï und Lin-Chen Kin, *Compt. rend.*, **209**, 221 u. 346 (1939), **212**, 242 u. 268 (1941).
12) *DMS-Kartei*, S-Karte Nr. 3423.
13) J. A. McRae, R. B. VanOrder, F. H. Grifith und Th. E. Habgood, *Canadian J. Chem.*, **29**, 482 (1951).
14) F. E. King und T. J. King, *J. Chem. Soc.*, **1942**, 726.

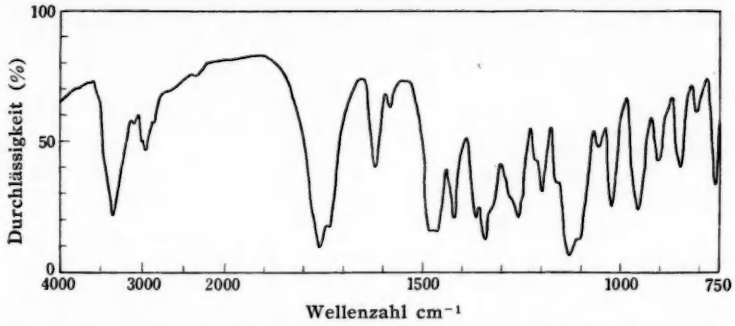


Abb. 1. IR-Absorption der 3.4.5-Trimethoxy-*o*-phthalaldehydsäure (Fp. 129°C).

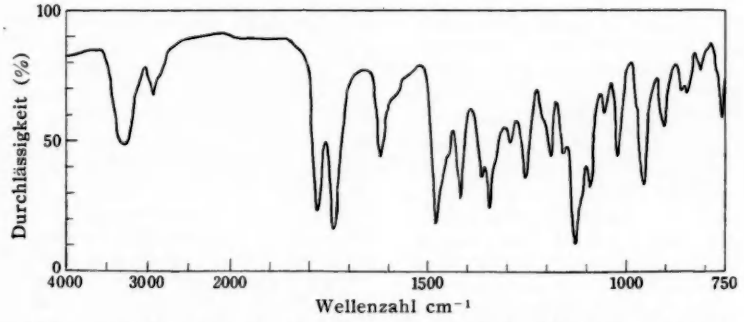


Abb. 2. IR-Absorption der 3.4.5-Trimethoxy-*o*-phthalaldehydsäure (Fp. 135°C).

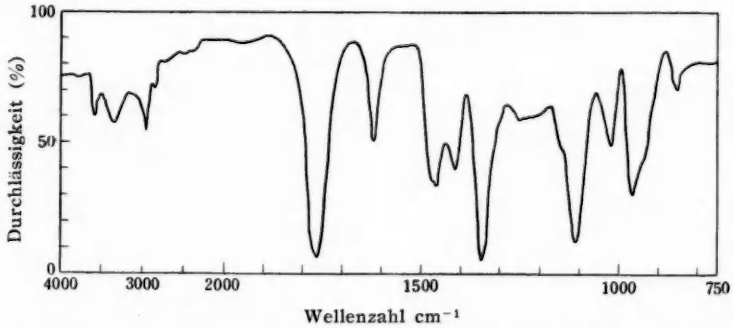


Abb. 3. IR-Absorption der 3.4.5-Trimethoxy-*o*-phthalaldehydsäure (in Chlf.).

Kristallarten von den Schmelzpunkten 114 und 124°C, deren Unterschied nach den IR-Spektren auf dem der Kristallstruktur beruhen muß. Ein Molekül der Verbindung XVI besitzt insgesammt 5 aktive Wasserstoffatome, und seine Reaktionen mit überschüssigem NBS sind sehr komplex; sie werden weiter untersucht.

Die Ergebnisse der NBS-Oxydation der Polymethoxyphthalide sind zusammenfassend in der Tabelle I angegeben.

Aus Phthalaldehydsäure wurden 3-Alkylphthalide durch Grignardreaktion mit Alkylmagnesiumjodiden in guter Ausbeute hergestellt[15,16] und andere kernsubstituierte 3-Alkylphthalide können auch auf diese Weise aus den entsprechenden substituierten Phthalaldehydsäuren gewonnen werden[1,16]. Bei den polymethoxylierten

15) H. Simonis, E. Marben und E. Mermod, *Ber. dtsch. chem. Ges.*, **38**, 3981 (1905).
16) E. Mermod und H. Simonis, ebenda, **41**, 982 (1908).

TABELLE I. NBS-OXYDATION DER POLYMETHOXYPHTHALIDE

Phthalid	Produkte	
	Phthalid : NBS=1 : 1 (°C)	Phthalid : NBS=1 : 2 (°C)
I	II, Fp. 129 u. 135 (77%)[a]	III, Fp. 174,5[b] (51%) u. daneben II (16%)
IV	V, Fp. 98,5 (85%)[c]	VI, Fp. 192,3 (87%)
VII[d]	VIII, Fp. 147,5[e] (81%)	IX, Fp. 187[f] (56%) u. daneben VIII (32%)
X[d]	XI, Fp. 184[g] (48%)	XII, Fp. 204[h] (28%) u. daneben XI (55%)
XIII	XVI, Fp. 136[i] (53%)	III, Fp. 174 (43%)
XV	XVI, Fp. 114 u. 124 (50%)	

a) In Klammern Ausbeute; b) G. Bargellini u. a., *Atti Acad. Lincei*, **21 II**, 146 (1912), Fp. 174°C; c) Daten aus Lit. 1 zitiert; d) Lösungsmittel Benzol u. CCl_4 (1 : 2 in Volumen); e) Lit. 2, Fp. 150°C; f) Lit. 2, Fp. 187°C; g) Lit. 8, Fp. 187~188°C; h) R. G. Fargher u. a., *J. Chem. Soc.*, **119**, 1724 (1921), Fp. 202°C; i) Lit. 8, Fp. 136°C, Mischprobe mit der höher schmelzenden II zeigte eine Depression von ca. 10°C.

Derivaten, besonders bie Opiansäure, nimmt die Ausbeute ab, offenbar weil die Löslichkeit von Polymethoxyphthalaldehydsäuren in Äther viel geringer ist. Es gelang uns also 3-Methyl-4.5.6-trimethoxyphthalid aus der ätherischen Suspension der höherschmelzenden Aldehydsäure II herzustellen. Die niedrigerschmelzende II war unter allen Bedingungen—soweit versucht—nicht fähig, mit Methylmagnesiumjodid zu reagieren. Der Unterschied der Reaktivität beider Kristallarten, der auch auf dem der Kristallstruktur beruhen mag, ist jedoch noch nicht völlig aufgeklärt.

Organische Bromide können auch aus den entsprechenden um ein Kohlenstoffatom höheren Carbonsäuresilbersalzen durch Behandeln mit Brom hergestellt werden[17,18]. Um andere Möglichkeiten zur Darstellung der 3-Bromphthalide und dadurch die der Darstellung der Phthalaldehydsäuren zu finden, wurde nun die Reaktion des Silbersalzes der aus 3-Trichlormethyl-4.5.6-trimethoxyphthalid hergestellten 4.5.6-Trimethoxyphthalid-3-carbonsäure (XVII)[19] mit Brom probiert. Obgleich XVII in einer äquimolekularen Kalilauge beim Versetzen mit Silbernitrat kein Silbersalz ausfallen läßt, ergibt sie jedoch in einer wässerigen Lösung, die die zweifach-molekulare Menge Kaliumhydroxyd enthält, beim Zusatz des Silbernitrats Disilbersalz der 2-(Hydroxy-carboxy-methyl)-3.4.5-trimethoxybenzoesäure. Da Silbersalze aromatischer Carbonsäuren nach unseren Versuchen im allgemeinen langsamer als Salze aliphatischer Säuren mit Brom unter Decarboxylieren reagieren und da Salze der α-Hydroxycarbonsäuren Aldehyde geben[20], wird das Disilbersalz mit einer äquimolekularen Menge Brom in Tetrachlorkohlenstoff behandelt, wobei 4.5.6-Trimethoxy-7-bromphthalid-3-carbonsäure (XVIII) statt der erwarteten Aldehydsäure II erhalten wird. XVIII enthält ein Molekül Kristallwasser und gibt das Wasser beim Schmelzen ab. Eine andere Konstitutionsmöglichkeit, nämlich 2-(Hydroxy-carboxy-methyl)-3.4.5-trimethoxy-6-brombenzoesäure, wird aber nach dem IR-Absorptionsspektrum, wegen des undeutlichen Schmelzpunktes sowie auf Grund der Tatsache, daß die wasserfreie Säure XVIII viel höher schmilzt als die wasserhaltige, verneint. Die kristallwasserfreie Säure XVIII geht beim Erhitzen in 4.5.6-Trimethoxy-7-bromphthalid über. Die Totalausbeute beträgt auf XVII bezogen ca. 50%. Derselbe Bromphthalid wird auch aus 4.5.6-Trimethoxy-7-aminophthalid, der aus XVII über 4.5.6-Trimethoxyphthalid und 4.5.6-Trimethoxy-7-nitrophthalid hergestellt wurde[1], nach Sandmeyer hergestellt, wobei die Ausbeute auf XVII bezogen höchstens 5% beträgt.

Beschreibung der Versuche

1. 4.5.6-Trimethoxyphthalid (I)[14].—Ein Gemisch aus 10 g Gallussäuretrimethyläther, 33 ccm 30%-igem Formalin und 9 ccm konz. Salzsäure wurde 20 Min. am Rückfluß erhitzt, 5 g (47%) farblose Nadeln, Fp. 136°C** (aus Äthanol) (Lit.[14] 135~136°C).

2. 4.5.6.7-Tetramethoxyphthalid (IV)[1]. — Eine Lösung von 10 g 3.4.5.6-Tetramethoxyphthalalkohol in 60 ccm Eisessig wurde mit einer Lösung von 8 g Natriumbichromat in 60 ccm Eisessig bei 60°C tropfenweise oxydiert, 3,5 g

17) A. Lüttringhaus und D. Schade, ebenda, **74B**, 1565 (1941).
18) H. Hunsdiecker und Cl. Hunsdiecker, ebenda, **75B**, 291 (1942).
19) R. L. Alimchandani, *J. Chem. Soc.*, **125**, 540 (1924).
20) J. Kleinberg, *Chem. Revs.*, **40**, 381 (1947).
** Schmelzpunkte wurden mikroskopisch bestimmt, aber nicht korrigiert.

(36%) leicht gelbe Nadeln, Fp. 52°C (aus Äther) (Lit.[1] 52°C).

3. Mekonin (VII)[2].—Ein Gemisch aus 8 g 2.3-Dimethoxybenzoesäure, 35 ccm konz. Salzsäure und 30 ccm 30%-igem Formalin wurde 15 Min. am Rückfluß erhitzt, 2 g (24%) farblose Nadeln, Fp. 101～103°C (aus Wasser) (Lit.[2] 102°C).

4. *m*-Mekonin (X)[13].—50 g Veratrumsäure wurden in 250 ccm Eisessig mit 80 ccm 40%-igem Formalin und 200 g konz. Salzsäure 10 Std. auf 90～95°C und noch 3 Std. auf 100°C erhitzt. 25 g (47%) farblose Nadeln, Fp. 155°C (aus Wasser) (Lit.[13] 155°C).

5. 5. 6. 7-Trimethoxyphthalid (XIII)[13].—20 g X wurden durch Versetzen mit 10 ccm konz. Schwefelsäure und 140 ccm konz. Salpetersäure zu 8 g 7-Nitro-*m*-mekonin nitriert, dessen Reduktion in Essigester mit Raney-Nickel 6,5 g 5.6-Dimethoxy-7-aminophthalid [Fp. 181～182°C (aus Äthanol)] ergibt. 5,9 g des Hydrochlorids dieses Amins geben durch Diazotieren mit Natriumnitrit und durch anschließendes Versetzen mit Kaliumjodid 3,5 g 5.6-Dimethoxy-7-jodphthalid [Fp. 169°C (aus Essigsäure)], dessen 3,2 g bei 12-stündigem Kochen in einer methanolischen Lösung von 0,8 g Kalium in Gegenwart von wenig Kupferbronze (Merck) in 2,0 g XIII übergehen, Fp. 136～136,5°C (aus Wasser) (Lit.[13] 136,6～137°C). Mischprobe mit I zeigte eine Depression von ca. 10°C.

6. 4. 5. 6-Trimethoxy-7-chlormethylphthalid[14].—Ein Gemisch aus 10 g Gallussäuretrimethyläther, 33 ccm 30%-igem Formalin und 40 ccm konz. Salzsäure 20 Min. am Rückfluß erhitzt, 6,5 g (51%) farblose Nadeln, Fp. 85°C (aus Äthanol) (Lit.[14] 85°C).

7. 4.5.6-Trimethoxy-7-methylphthalid (XV).—5 g der vorstehenden Chlormethylverbindung wurden in 70 ccm Eisessig mit 13,5 g Zinkstaub 30 Min. am Rückfluß gekocht, das Filtrat nach dem Erkalten im Vakuum eingeengt und dann mit Wasser versetzt. Der ausgeschiedene Niederschlag wurde aus verdünnter Essigsäure umkristallisiert, 4,4～4,5 g (ca. 90%) farblose Nadeln, Fp. 80～82°C.

*Anal.**** Gef.: C 58,07; H 5,88. Ber. für $C_{12}H_{14}O_5 \cdot 1/2CH_3CO_2H$ (268,2): C 58,20; H 6,01.

8. 3. 4. 5-Trimethoxyphthalaldehydsäure (II).—4 g I wurden in 350 ccm Tetrachlorkohlenstoff mit 3,2 g NBS in Gegenwart von einer Messerspitze Dibenzoylperoxyd (abgekürzt BPO) unter Bestrahlung mit einer 500W-Wolframlampe 1 Std. am Rückfluß gekocht. Das gebildete Succinimid wurde abgesaugt und das Filtrat eingeengt. Der Rückstand wurde mit ca. 150 ccm Wasser unter mechanischem Rühren 2 Std. auf dem siedenden Wasserbad erwärmt, das Reaktionsgemisch abfiltriert und die Lösung langsam abdunsten gelassen. Dabei fielen gelbe Nadeln aus, Ausbeute 3,4 g (77%), Fp. 128,5～129°C (aus Wasser) und Fp. 134～135°C (aus Äthanol oder Chloroform).

Anal. Gef.: C 55,13; H 5,11. Ber. für $C_{11}H_{12}O_6$ (240,2): C 55,00; H 5,04.

2.4-Dinitrophenylhydrazon.—Orange Nadeln, Fp. 235～236°C (aus 95%-igem Äthanol).

Anal. Gef.: C 48,73; H 4,13; N 13,28. Ber. für $C_{17}H_{16}N_4O_9$ (420,4): C 48,58; H 3,84; N 13,33.

9. 3. 4. 5-Trimethoxyphthalsäure (III).—11,2 g I wurden in 1000 ccm Tetrachlorkohlenstoff mit 18 g NBS und wenig BPO 1 Std. unter Bestrahlung am Rückfluß gekocht, das gebildete Succinimid abgesaugt und das Filtrat eingeengt. Der Rückstand wurde mit 150 ccm Wasser 2 Std. auf dem siedenden Wasserbad erwärmt und das Gemisch noch heiß abfiltriert. Es fielen zuerst 1,3 g (16%) II beim Abkühlen der Lösung und dann 6,6 g (51%) III beim Einengen der Mutterlauge in Prismen aus, Fp. 173,5～174,5°C (aus Wasser) (Lit.[10] 174°C), IR-Absorption in KBr: 1680～1720 cm^{-1} (breite Bande).

Anhydrid.—Nadeln, Fp. 143～144°C (aus Benzol) (Lit.[10] 143°C), IR-Absorptionen in KBr: 1724 u. 1831 cm^{-1}.

2.4-Dinitrophenylhydrazon des Anhydrids.—Gelbe Nadeln, Fp. 254,5～256°C (aus Äthanol).

Anal. Gef.: C 49,00; H 3,73; N 13,79. Ber. für $C_{17}H_{14}N_4O_9$ (418,3): C 48,81; H 3,37; N 13,39.

10. 3.4.5.6-Tetramethoxyphthalsäure (VI).—1,5 g IV wurden in 30 ccm Tetrachlorkohlenstoff mit 2,1 g NBS und wenig BPO unter Bestrahlung 1 Std. am Rückfluß gekocht und das Gemisch wie vorstehend aufgearbeitet, wobei 1,3 g (86%) VI in farblosen Nadeln erhalten wurden. Fp. 191,7～192,3°C (aus Wasser), IR-Absorption in KBr: 1690～1710 cm^{-1} (breite Bande).

Anal. Gef.: C 50,43; H 5,00. Ber. für $C_{12}H_{14}O_8$ (286,2): C 50,35; H 4,93.

Anhydrid bildete sich beim Schmelzen von VI quantitativ, Fp. 137,5～138°C (aus Benzol).

Anal. Gef.: C 53,50; H 4,75. Ber. für $C_{12}H_{12}O_7$ (268,2): C 53,73; H, 4,51.

2.4-Dinitrophenylhydrazon des Anhydrids.—Gelbe Nadeln, Fp. 220,5～221°C (aus Äthanol).

Anal. Gef.: C 48,58; H 3,86; N 12,41. Ber. für $C_{18}H_{16}N_4O_{10}$ (448,4): C 48,22; H 3,60; N 12,50.

11. 3. 4. 5-Trimethoxy-6-methylphthalaldehydsäure (XVI).—Eine Lösung von 2 g XV in 150 ccm Tetrachlorkohlenstoff wurde mit 2 g NBS und wenig BPO unter Bestrahlung 2 Std. am Rückfluß erhitzt und das Gemisch wie vorstehend aufgearbeitet, 0,98 g (50%) farblose Nadeln, Fp. 114°C (aus Wasser), IR-Absorptionen in KBr: 1690 u. 1703 cm^{-1}, und Fp. 122°C (aus Chloroform), IR-Absorptionen in KBr: 1689 u. 1703 cm^{-1}.

Anal. Gef.: C 56,44; H 4,88. Ber. für $C_{12}H_{14}O_6$ (254,2): C 56,69; H 4,55.

2.4-Dinitrophenylhydrazon.—Rote Nadeln, Fp. 214°C (aus 95%-igem Äthanol und Essigester).

Anal. Gef.: C 50,02; H 3,86; N 12,84. Ber. für $C_{18}H_{18}N_4O_9$ (434,4): C 49,72; H 4,12; N 12,89.

12. 3-Methyl-4. 5. 6-trimethoxyphthalid.—Einem Grignardreagens aus 0,50 g Magnesiumspänen und 3,0 g Methyljodid wurde eine Suspension von 1,5 g II vom Fp. 135°C in 500 ccm absolutem Äther unter Eiskühlung zugetropft. Es wurde 1 Std. unter Eiskühlung und noch 1 Std. am Rückfluß umgerührt. Das Reaktionsgemisch wurde auf Eis gegossen und mit 2 N Schwefelsäure angesäuert. Die wässerige Schicht wurde mehrmals mit Äther ausgezogen, die ätherische Lösung mit verdünnter Natriumhydrogencarbonatlösung

*** Für Mikroanalysen der Verbindungen sind wir der Zentralen Mikroanalysenstelle der Univ. Kyōto sehr dankbar.

gewaschen, mit Natriumsulfat getrocknet und eingeengt. Es blieb ein gelbes Fett zurück, das aus Wasser kristallisiert wurde, 0,75 g (49%) farblose Nadeln, Fp. 52°C, IR-Absorption in KBr: 1765 cm^{-1}.

Anal. Gef.: C 60,56; H 5,98. Ber. für $C_{12}H_{14}O_5$ (238,2): C 60,50; H 5,92.

13. 2.4-Dinitrophenylhydrazon des Phthalsäureanhydrids. — Gelbe Nadeln, Fp. 280~282°C (aus 95%-igem Äthanol und Essigester).

Anal. Gef.: C 51,09; H 2,62; N 17,65. Ber. für $C_{14}H_8N_4O_6$ (328,2): C 51,23; H 2,46; N 17,07.

14. 4. 5. 6-Trimethoxyphthalid-3-carbonsäure (XVIII)[20]. — 5 g 3-Trichlormethyl-4. 5. 6-trimethoxyphthalid wurden in einer Natronlauge aus 5 g Natriumhydroxyd und 20 ccm Wasser 45 Min. erhitzt und das abgekühlte Gemisch mit Salzsäure angesäuert, 3,5 g (90%) farblose Nadeln, Fp. 147~148°C (aus Wasser) (Lit.[20] 147~148°C).

15. Disilbersalz der 2-(Hydroxy-carboxy-methyl)-3. 4. 5-trimethoxybenzoesäure. — Eine Lösung von 2,68 g XVII in einer Kalilauge aus 1,12 g Kaliumhydroxyd und 100 ccm Wasser wurde mit 3,4 g Silbernitrat in 100 ccm Wasser versetzt. Der Niederschlag wurde mit Methanol gewaschen und im Vakuumexsikkator getrocknet, 3,04 g (76%).

Anal. Gef.: Ag 42,75. Ber. für $C_{12}H_{12}Ag_2O_8$ (499,8): Ag 43,18.

16. 4. 5. 6-Trimethoxy-7-bromphthalid-3-carbonsäure (XVIII).—Eine Suspension von 3,0g vorstehenden Silbersalzes in 100 ccm Tetrachlorkohlenstoff wurde bei ihrem Siedepunkt mit 1,2 g Brom in 20 ccm Tetrachlorkohlenstoff tropfenweise versetzt, das Gemisch mit 150 ccm 0,1 N Brom-Wasserstoffsäure 10 Min. umgerührt und das Silberbromid abfiltriert (2,70 g). Beim Einengen des Filtrats fielen farblose Nadeln aus, 3,50 g (90%), Fp. 75~90°C (aus Wasser). IR-Absorptionen in KBr: 1721 cm^{-1} (COOH) u. 1761 cm^{-1} (Phthalid).

Anal. Gef.: C 39,81; H 3,84; Br 22,04. Ber. für $C_{12}H_{11}BrO_7 \cdot H_2O$ (365,1): C 39,49; H 3,59; Br 21,89.

Beim Schmelzen bildete sich die wasserfreie XVIII, Fp. 137~138°C.

Anal. Gef.: C 41,40; H 3,32; Br 23,27. Ber. für $C_{12}H_{11}BrO_7$ (347,1): C 41,55; H 3,19; Br 23,02.

17. 4. 5. 6-Trimethoxy-7-bromphthalid (XIX).— 2,92 g der wasserfreien XVIII wurden auf 185°C erhitzt, 1,91 g (76%) (nach einer Umkristallisation aus Methanol), Fp. 103~104°C.

18. XIX aus 4. 5. 6-Trimethoxy-7-aminophthalid. —Eine Lösung von 4 g 4.5.6-Trimethoxy-7-aminophthalid[19] in 3 ccm konz. Schwefelsäure und 20 ccm Wasser wurde mit 2 g festem Natriumnitrit diazotiert, die überschüssige salpetrige Säure mit Harnstoff zersetzt, das Gemisch mit 2,4 g Kupfer(I)-bromid mit überschüssiger Bromwasserstoffsäure versetzt und dann erhitzt. Das dabei getrennte Öl wurde nach dem Erkalten aus Methanol kristallisiert, 1,5 g (29%), farblose Nadeln, Fp. 103~104°C. Mischschmelzpunkt mit dem obenstehenden Präparat 103~104°C.

Zusammenfassung

Polymethoxyphthalaldehydsäuren wurden aus den entsprechenden Phthaliden durch Bromieren mit äquimolekularer Menge an NBS und durch anschließende Hydrolyse der Produkte in guten Ausbeuten hergestellt, während die Verwendung von überschüssigem Reagens Phthalsäuren ergab. 3. 4. 5-Trimethoxyphthalaldehydsäure existiert in Chloroformlösung als 3-Hydroxy-4. 5. 6-trimethoxyphthalid und fällt aus den Lösungen als echte Phthalaldehydsäure in zwei verschiedenen Kristallarten aus, von denen nur die höher schmelzende durch Grignardreaktion mit Methylmagnesiumjodid 3-Methyl-4. 5. 6-trimethoxyphthalid ergeben konnte. Das aus 4. 5. 6-Trimethoxyphthalid-3-carbonsäure hergestellte Disilbersalz ergab durch Versetzen mit Brom statt der erwarteten Phthalaldehydsäure das 7-Bromderivat.

Herrn Prof. Dr. F. Weygand, München sagen wir an diesser Stelle unseren aufrichtigsten Dank für seine Anleitung und Anregung zu vorstehender Arbeit. Dem Unterrichtsministerium Japan sind wir für seine Unterstützung dieser Arbeit durch eine Beihilfe für individuelle Forschung 1958 zum Dank verpflichtet.

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Studies on the Cobalt(III) Complexes of Monothiophosphate Ion

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(Received June 11, 1959)

Recently, Yasuda and Lambert[1] reported that the monothiophosphate ion shows an interesting color reaction with the cobalt-(II) ion in aqueous solution. Except for this report there has been no description heretofore about the coordinative nature of the monothiophosphate ion. In the present paper, the syntheses of di-monothiophosphato - bis - ethylenediamine and monothiophosphato - bis - ethylenediamine cobalt(III) complexes will be reported. Furthermore, their visible and ultraviolet and also the infrared absorption spectra will be discussed mainly in comparison with those of the known thiosulfato complexes of cobalt(III).

Experimental

Preparation.—*1) Dark green complex*: $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O$. — This complex was prepared as follows: 3.2 g. anhydrous sodium monothiophosphate[1,2], was completely dissolved in 80 ml. of water, and the solution was added to the aqueous solution (20 ml.) of 2.5 g. *trans*-$[Co\,en_2Cl_2]Cl$. The color of the mixture changed from dark red to dark greenish red. To complete the reaction the mixture was preserved for one hour. The resulting solution was filtered quickly, and ethanol was added carefully to the clear filtrate on cooling. Dark greenish crystalline powder was obtained. The crude product was recrystallized from a small quantity of cold water by the addition of ethanol. The fine crystals obtained were dried in a desiccator over sulfuric acid.

Anal. Found: Co, 9.58; P, 9.72; N, 8.97; C, 7.67; H, 5.05; H_2O, 23.66. Calcd. for $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O = C_4H_{16}O_6S_2N_4P_2Na_3Co\cdot 8H_2O$: Co, 9.59; P, 10.10; N, 9.12; C, 7.82; H, 5.25; H_2O, 23.46%.

2) Dark red complex: $[Co\,en_2(SPO_3)]\cdot 2H_2O$.— To the aqueous solution (30 ml.) of 5 g. *trans*-$[Co\,en_2Cl_2]Cl$, was added on cooling an aqueous solution (70 ml.) of 3.2 g. of anhydrous sodium monothiophosphate. The resulting solution was dark red. A large amount of ethanol was added carefully to the solution. The desired complex was obtained as dark reddish crystalline powder.

Anal. Found: Co, 17.8; P, 9.35; N, 16.93; C, 14.37; H, 6.51; H_2O, 11.82. Calcd. for $[Co\,en_2(SPO_3)]\cdot 2H_2O = C_4H_{16}O_5SN_4PCo\cdot 2H_2O$: Co, 18.07; P, 9.5; N, 17.18; C, 14.73; H, 6.19; H_2O, 11.05%.

Measurements. — The visible and ultraviolet absorption measurements were made by a Beckman DU spectrophotometer in cold aqueous solutions to prevent the aquation of the complexes. The concentration of the solutions varied from $1/2\times10^{-2}$ to $1/8\times10^{-3}$ F. The infrared spectra were obtained by a Parkin-Elmer Model 21 (double beam) and a Hilger H-800 infrared spectrophotometer using sodium chloride prisms. The potassium bromide disk method and nujol mull technique were employed.

Materials.—Thiosulfato-pentammine cobalt(III) chloride, $[Co(NH_3)_5(SSO_3)]Cl$[3], and sodium dithiosulfato - bis - ethylenediamine cobaltate(III), $Na[Co\,en_2(SSO_3)_2]$[4], were obtained as dark red and green crystals, respectively, in the usual way as done by Rây and his coworker. The visible and ultraviolet absorption curves of these compounds are shown in Figs. 1 and 2. These absorption curves were in good agreement with those obtained by Kiss et al.[5,6].

Results and Discussion

Dark green complex: $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O$.—The visible and ultraviolet absorption curve of this compound is shown in Fig. 1, in which the spectrum of the corresponding thiosulfato-complex, $Na[Co\,en_2(SSO_3)_2]$, is also plotted for comparison. These two absorption curves are similar to each other on the whole. The frequencies of the absorption maxima for each complex are listed in Table I.

The first absorption bands of these complexes are shifted towards longer wavelengths than those of complexes of $[Co^{III}N_4O_2]$ type[7,8] and distinctly split into two components. Moreover, the type of these splittings differ from those of $[Co^{III}N_4O_2]$ and $[Co^{III}N_5O]$ type complexes.

1) S. K. Yasuda and J. L. Lambert, *J. Chem. Educ.*, **31**, 572 (1954).
2) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8, Longmans, Green & Co., New York (1931), p. 1068—1069.
3) P. R. Rây, *J. Indian Chem. Soc.*, **4**, 71 (1927).
4) P. R. Rây and S. N. Maulik, ibid., **10**, 655 (1933).
5) A. Kiss and D. Czeglédy, *Z. anorg. u. allgem. Chem.*, **235**, 407 (1938).
6) A. Kiss, G. Auer and E. Major, ibid., **264**, 28 (1941).
7) M. Linhard and M. Weigel, ibid., **264**, 321 (1951).
8) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

TABLE I. THE FIRST, SECOND AND THE CHARGE-TRANSFER BANDS OF MONOTHIOPHOSPHATO AND THIOSULFATO Co(III) COMPLEXES
(in frequency unit 10^{13}/sec.)

Complex salt	First band ν_{max} (log ε)	Second band ν_{max} (log ε)	Charge-transfer band ν_{max} (log ε)
$[Co(NH_3)_5(SSO_3)]Cl$	58.8 (1.82)	ca. 82 (2.3)	103.4 (4.9) 126 (3.6)
$Na[Co\,en_2(SSO_3)_2]$	54.9 (1.93)		89.6 (4.28)
$Na_3[Co\,en_2(SPO_3)_2]$	53.9 (2.10)		87.0 (4.36) 108 (3.83)
$[Co\,en_2(SPO_3)]$	56.0 (2.31)	ca. 82 (2.6)	107.3 (4.16)

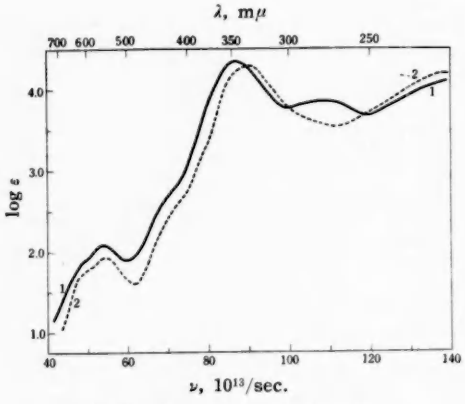

Fig. 1. Absorption spectra of:
1, $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O$;
2, $Na[Co\,en_2(SSO_3)_2]$.

These facts indicate that the cobalt(III) ion in these complex ions coordinates monothiophosphate or thiosulfate ions by their sulfur atoms. This conclusion is also supported by the fact that these complexes show intense absorption bands in the near ultraviolet, which are probably originated from charge transfer between the central cobalt(III) ion and the coordinated monothiophosphate or thiosulfate ion. As to the charge transfer band of di-thiosulfato-bis-ethylenediamine cobalt(III) ion, it is located at a longer wavelength than that of thiosulfato-pentammine cobalt(III) ion. Judging from the position of the thiosulfate ion in the spectrochemical series, it is evident that $[Co\,en_2(SSO_3)_2]^-$ has *trans* structure with regard to two thiosulfate ions in coordination[8]. It may be concluded, therefore, that the structure of $[Co\,en_2(SPO_3)_2]^{3-}$ is also *trans*, since its absorption curve is quite similar to the corresponding thiosulfato-complex.

Structure of the Dark Red Complex.—From the result of the chemical analysis, there was two possibilities of the structure of the "dark red complex". The one is $[Co\,en_2(OH_2)(SPO_3)]\cdot H_2O$ in which the monothiophosphate ion is coordinated as a monodentate ligand, and the other, $[Co\,en_2(SPO_3)]\cdot 2H_2O$ in which the monothiophosphate ion is coordinated as a chelate ligand.

Being heated for dehydration, sodium di-monothiophosphato-bis-ethylenediamine cobaltate(III) is rather unstable and changes into black sulfide of cobalt at about 110°C with evolution of hydrogen sulfide. On the contrary, the dark red complex is more stable against heating. Even after the two molecules of water were expelled at 110°C, the dark red color of the complex was well preserved and no indication of the decomposition of the complex was observed. These facts suggest that the structure of the dark red complex is $[Co\,en_2(SPO_3)]\cdot 2H_2O$ and not $[Co\,en_2(OH_2)(SPO_3)]\cdot H_2O$.

The visible and ultraviolet absorption curve of the dark red complex is shown in Fig. 2, in which the spectrum of thiosulfato-pentammine cobalt(III) ion is also plotted for comparison.

The trend that the two absorption curves resemble each other on the whole, is similar to the case of Fig. 1. There are, however, a few important differences between the two curves in Fig. 2. In the

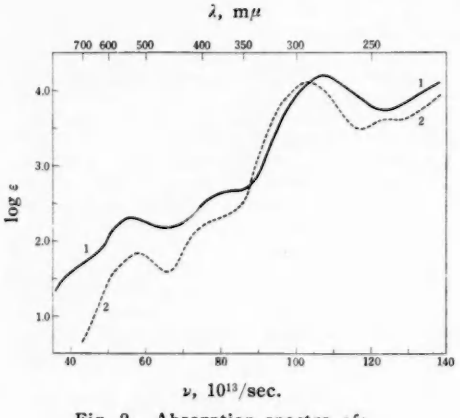

Fig. 2. Absorption spectra of:
1, $[Co\,en_2(SPO_3)]\cdot 2H_2O$;
2, $[Co(NH_3)_5(SSO_3)]Cl$.

first place, the charge transfer band of the dark red complex ($\nu = 107.3 \times 10^{13}$/sec.) is in a shorter wavelength than that of the thiosulfato-pentammine complex. The second difference is seen in the first and the second absorption bands. In this region, the absorption of the dark red complex is stronger in intensity than that of the thiosulfato-pentammine complex. These phenomena may be considered as a proof for the structural difference between the two complexes, especially the difference in the type of coordination of the sulfur-containing ligands.

Infrared Absorption Spectra. — Fig. 3 indicates the infrared spectra of the thiosulfato cobalt(III) complexes and of sodium thiosulfate pentahydrate in 1250~850 cm^{-1} region. Except for the absorption bands which are due to the vibration of ethylenediamine, two absorption bands appear in this region, which are assigned as the S-O vibration[9].

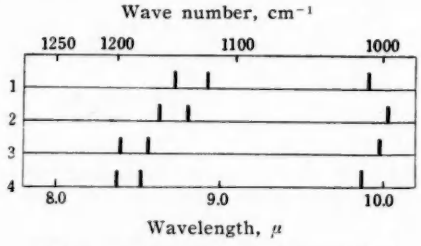

Fig. 3. Infrared absorption bands of:
1, $Na_2S_2O_3 \cdot 5H_2O$ (KBr disk);
2, $[Co(NH_3)_5(SSO_3)]Cl$ (nujol mull);
3, $Na[Co\,en_2(SSO_3)_2]$ (nujol mull);
4, $K_4[Co(CN)_5(SSO_3)]$ (KBr disk).

The free thiosulfate ion has the symmetry of C_{3v}, and the symmetry is not altered by coordination, because the central cobalt(III) ion is attached to the sulfur atom of the monodentate thiosulfate ion in these complexes. As is seen in Fig. 3, although the band at 1000 cm^{-1} is hardly shifted by coordination, the bands at 1120 cm^{-1} are shifted to higher frequencies by coordination. A similar trend is seen in the cobalt(III) complex which contains monothiophosphate ions as monodentate ligand (Fig. 4).

These facts will be explained from the assumption that the free ligand (SPO_3^{3-}) and the coordinated ligand have the same symmetry C_{3v}. The two sharp bands of the free ligand are due to the PO_3 group

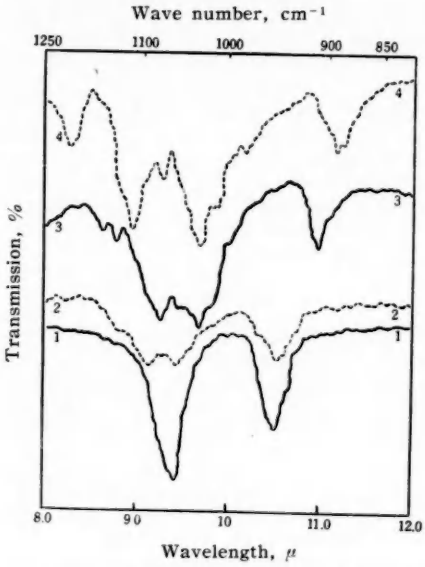

Fig. 4. Infrared absorption spectra of:
1, Na_3SPO_3 (KBr disk);
2, $Na_3[Co\,en_2(SPO_3)_2] \cdot 8H_2O$ (KBr disk);
3, $[Co\,en_2(SPO_3)] \cdot 2H_2O$ (nujol mull);
4, $[Co\,en_2(SPO_3)]$ (nujol mull).

and the vibrations are assumed to be symmetric PO_3 stretching vibration (950 cm^{-1}) and degenerate PO_3 asymmetric vibration (1064 cm^{-1}), respectively[10]. In the di-monothiophosphato-bis-ethylenediammine cobalt(III) ion, the band at 950 cm^{-1} is hardly shifted, but the band at 1064 cm^{-1} is shifted to a higher frequency and splits into two peaks. This trend is in good accordance with that of the thiosulfato complexes mentioned above. These relationships led us to the conclusion that the cobalt(III) ion in this complex coordinates the monothiophosphate ion by the sulfur atom, in good agreement with the conclusion from the visible and ultraviolet spectra. On the contrary, in the spectra of the dark red complex, the symmetric PO_3 stretching vibration of the monothiophosphate ion is shifted to a lower frequency by coordination. If it is assumed that the dark red complex has the structure containing the monodentate monothiophosphate ligand, namely, $[Co\,en_2(OH_2)(SPO_3)] \cdot H_2O$, the symmetry of the coordinated SPO_3^{3-} ions is C_{3v}, but if the chelate structure in $[Co\,en_2(SPO_3)] \cdot 2H_2O$, is assumed, the symmetry of the ligand is lowered to C_s. It is presumed, therefore,

9) K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4909 (1957).

10) M. Tsuboi, ibid., **79**, 1351 (1957).

that the shift of the band at 950 cm^{-1} is caused by the chelate coordination. Furthermore, in the spectra of the dehydrated complex (Fig. 4), no new band by degradation symmetry appears, though the bands are more or less shifted. These shifts probably result from the vanishing of the hydrogen-bond between the water molecules and the SPO_3^{3-} group. Similar shifts were reported for some inorganic phosphorus compounds[11].

Summary

Two new complexes, sodium di-monothiophosphato-bis-ethylenediamine cobaltate(III) octa-hydrate and monothiophosphato-bis-ethylenediamine-cobalt(III) dihydrate, have been synthesized by the reaction of *trans*-dichloro-bis-ethylenediamine cobalt(III) chloride with anhydrous sodium monothiophosphate in cold aqueous solution. The infrared and the visible and ultraviolet absorption spectra of these compounds and of the corresponding thiosulfato-Co(III) complexes have been measured and discussed in relation to the structures of the complexes.

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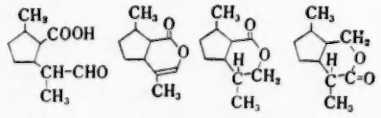
11) D. E. C. Corbridge and E. J. Lowe., *J. Chem. Soc.*, **1957**, 493.

The Synthesis of Cyclopentane Derivatives. I

By Tsuguo TANAKA

(Received April 11, 1959)

Recently, several methylcyclopentane derivative from natural sources have been reported. Among them, nepetalic acid (I) and nepetalactone (II) from the oil of cat-nip (Nepeta cataria)[1], matatabilactone (III) from the oil of the wormseed of matatabi (Actinidia poligama Miq.,)[2] and iridolactone (IV) from ant (Iridomyrmex species)[3] are particularly interesting because of their close relationship concerning both physiological activities and chemical structures.

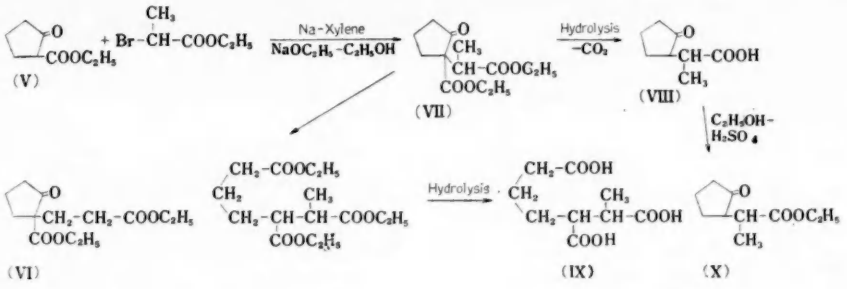


(I) (II) (III) (IV)

The determination of conformations of these compounds[4] in relation to their physical and chemical properties seems worthy of further considerations. Now, synthesis of several cyclopentane derivatives was attempted with a view to obtain some informations about conformational problems and to find out a new synthetic route.

In the present experiment, *cis*- and *trans*-lactones of 2-α-carboxyethylcyclopentanol were prepared as the first step in a series of this investigation attempted, which lead to the compounds having no methyl substituent in the ring, and thus alleviating stereochemical difficulties. The condensation of carbethoxycyclopentanone (V) with ethyl α-bromopropionate, reported by Šorm et al.[5] and Sen et al.[6], respectively, was re-examined and some new results were obtained. The condensation was conducted by use of either sodium metal in toluene[5,7] or sodium ethoxide in absolute alcohol[8]. 2-Carbethoxy-2-α-carbethoxyethyl cyclopentanone (VII) was obtained

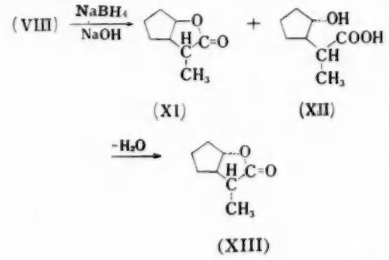
1) S. M. McElvain, R. D. Bright and P. R. Johnson, *J. Am. Chem. Soc.*, **63**, 1558 (1941); E. J. Eisenbraun and S. M. McElvain, ibid., **77**, 1599 (1955).
2) T. Sakan, A. Fujino, F. Murai, Y. Butsugan and A. Suzui, This Bulletin, **32**, 315 (1959).
3) G. W. K. Cavill, D. L. Ford and H. D. Locksley, *Chem. & Ind.*, **75**, 465 (1956).
4) R. B. Bates, E. J. Eisenbraun and S. M. McElvain, *J. Am. Chem. Soc.*, **80**, 3420 (1958); ibid., **80**, 3413 (1958).
5) F. Šorm, Z. Šormová and L. Šedivý, *Collection Czechoslov. Chem. Communs.*, **12**, 554 (1947); *Chem. Abstr*, **42**, 7742*c* (1948).
6) K. Sen and P. Bagchi, *Science and Culture (India)*, **20**, 254 (1954); *Chem. Abstr.*, **49**, 14652*e* (1955).
7) W. Herz. *J. Am. Chem. Soc.*, **78**, 1485 (1956).
8) (a) E. D. Bergmann and R. Ikan, ibid., **80**, 3135 (1958). (b) A. Kötz, *Ann.*, **350**, 235 (1906).



in 70 and 60% yield, respectively. Here, in the latter case, an acid, m. p. 147°C, was newly detected as the by-product of the cleavage of the ring in VII[9,8b] followed by hydrolysis of the ester group. The acid was identified as hexane-tricarboxylic acid-1,4,5 (IX) obtained by Sen et al.[10] from 2-methyl-2,3-dicarbethoxy-cyclohexanone; the formation substantiates structure VII for the condensation product.

2-Carbethoxy-2-β-carbethoxyethyl-cyclopentanone (VI) which might be the product of dehydrobromination and Michael addition[11] of ethyl α-bromopropionate to carbethoxycyclopentanone (V) could not be detected. The ketoester (VII) was converted into 2-α-carboxyethyl-cyclopentanone (VIII), m. p. 66°C, which on esterification yielded ethyl ester (X), as indicated in the formulation.

On the other hand, VIII was treated with sodium borohydride, when a selective reduction of the keto group[12] was realized;



from the reduction product a lactone of possibly *cis*-2-α-carboxyethyl-cyclopentanol (*cis*-lactone) (XI) and a hardly lactonized one, possibly *trans*-hydroxyacid (XII) were obtained. Structure XII was ascertained by analysis and also by the comparison of the absorption spectrum of the reduction product with that of keto-acid (VIII). 288 mμ band in the ultraviolet spectrum and 5.80 μ peak in the infrared spectrum of the keto-acid were not observed in the spectrum of the reduction product as illustrated in Figs. 1 and 2, respectively.

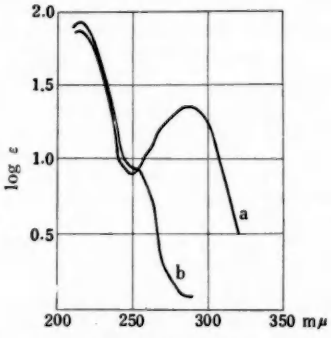


Fig. 1. Ultraviolet spectra of 2-α-carboxyethyl-cyclopentanone (a) and *trans*-2-α-carboxyethyl-cyclopentanol (b) in alcoholic solutions.

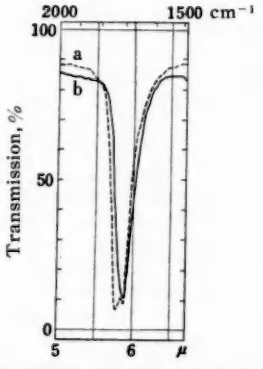


Fig. 2. Infrared spectra of 2-α-carboxyethyl-cyclopentanone (a) and *trans*-2-α-carboxyethyl-cyclopentanol (b).

9) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, **1934**, 964.
10) K. Sen and P. Bagchi, *Science and Culture (India)*., **19**, 312 (1953); *Chem. Abstr.*, **49**, 2338*f* (1955).
11) P. B. Talukdar and P. Bagchi, *J. Org. Chem.*, **20**, 25 (1955).
12) E. B. Reid and J. R. Siegel, *J. Chem. Soc.*, **1954**, 520; R. P. Zelinski, B. W. Turnquest and E. C. Martin, *J. Am. Chem. Soc.*, **73**, 5521 (1951).

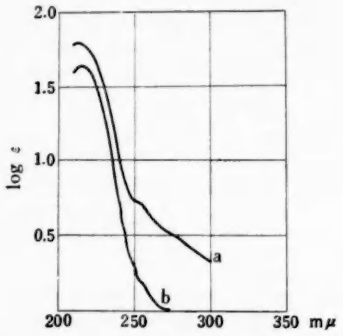


Fig. 3. Ultraviolet spectra of *trans*-lactone (a) and *cis*-lactone (b) in alcoholic solutions.

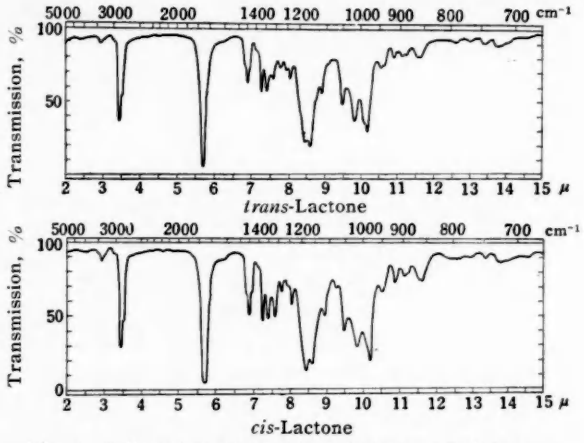


Fig. 4. Infrared spectra of *trans*-lactone and *cis*-lactone.

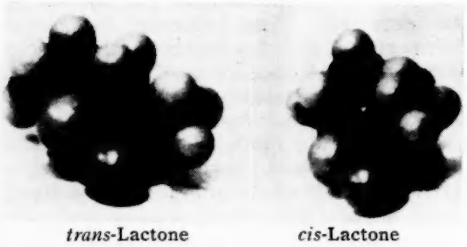
The reduction of 2-carboxymethyl-cyclopentanone with sodium amalgam in sodium hydroxide solution was reported by Linstead et al.[13] to yield *cis*-lactone in 28% yield. The lactonization of XII gave a sweet smelling *trans*-lactone (XIII) (heated under diminished pressure); a trace of concentrated sulfuric acid facilitated the reaction. In this way the reduction of keto-acid (VIII) yielded 37% of *cis*-lactone and 38% of *trans*-lactone (consult Table I).

TABLE I. PHYSICAL CONSTANTS OF *cis*- AND *trans*-LACTONES

	Density $d_4^{13.5}$	Refractive index $n_D^{13.5}$	b. p., °C
cis-Lactone	1.08462	1.4712	73~74/2 mm.
trans-Lactone	1.09688	1.4725	67/2 mm.

Some differences between these lactones were also revealed in the ultraviolet (Fig. 3) and infrared (Fig. 4) spectra of them. In the ultraviolet spectra, the extinction coefficient of *trans*-lactone is a little higher than that of *cis*-lactone particularly at longer wavelengths.

In the infrared spectra, comparison of relative intensity of absorption peaks 8.44 μ (a) and 8.60 μ (b) (C–O stretching) gives a convenient method of characterizing these lactones. In the spectra of *cis*- and *trans*- lactones, a>b and b>a are recognized, respectively. And the singlet absorption peaks 10.50 μ, 11.13 μ in the spectrum of *cis*-lactone, appear as doublet peaks 10.50, 10.64 μ; 11.13, 11.25 μ respectively in that of *trans*-lactone. By the examination of the molecular models in Fig. 5, it is ascertained that *cis*-lactone is a staggered molecule having *cis*-orientation at C_1 and C_2, while *trans*-lactone is a planar molecule having a *gauche*-orientation at C_1 and C_2.



trans-Lactone *cis*-Lactone

Fig. 5. The molecular models of *trans*-lactone and *cis*-lactone.

Experimental[14]

2-Carbethoxy-2-α-carbethoxyethyl-cyclopentanone.—(a) The Condensation of 73 g. of ethyl α-bromopropionate with 62 g. of 2-carbethoxy-cyclopentanone by use of 9.2 g. of sodium in 500 ml. of toluene was completed by refluxing the mixture for ten hours. The reaction product, being treated in the usual way, yielded 61 g. of fraction b. p. 128~129°C/2.5 mm., 7 g. of fraction b. p. 123~128°C/2.5 mm. The latter was also used for further work. Yield, 70%. λ_{max} 249 mμ log ε 3.09; ν_{max} 5.74 μ, 5.82 μ (C=O).

Anal. Found: C, 60.30; H, 7.85. Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25%.

2-α-Carboxyethyl-cyclopentanone. — Forty-five grams of 2-carbethoxy-2-α-carbethoxyethyl-cyclo-

13) R. R. Linstead and E. M. Mead, *J. Chem. Soc.*, **1934**, 935.

14) Infrared spectra were measured with Perkin Elmer Model 21 spectrophotometer and ultraviolet spectra in alcoholic solutions with Beckman E. P. U. spectrophotometer.

TABLE II. PHYSICAL CONSTANTS OF 2-α-CARBOXYETHYL-CYCLOPENTANONE AND ITS DERIVATIVES

	b. p., °C	m. p., °C	Melting point of semi-carbazone °C	Melting point of 2,4-dinitro-phenylhydrazone °C	Boiling point of ethylester °C
Šorm et al.	154/15 mm.	—	188	—	81～83/0.5 mm.
Sen et al.	150/3 mm.	—	—	220	—
Experiment	118～119/0.4 mm.	66	189	220	93.5～94/3 mm.

pentanone was gently refluxed with 100 ml. of concentrated hydrochloric acid for sixteen hours at 135～145°C in an oil bath. The reaction mixture was cooled and extracted with ether. Benzene was added to the ether solution and the solvents were evaporated and the residue was vacuum-distilled. A portion (18.4 g.) of the acid b. p. 118～119°C/0.4 mm. was obtained. Yield, 64%. On standing in the ice box, it gradually crystallized; m. p. 45°C. Recrystallized from benzene-petroleum ether as feathery needles; m. p. 66°C, λ_{max} 214 mμ log ε 1.86, 288 mμ log ε 1.34; ν_{max} 5.80 μ, 5.90 μ (C=O).

Anal. Found: C, 60.72; H, 7.84. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75%.

An additional amount (ca. 1 g.) was obtained by evaporating the hydrochloric acid solution in vacuum and extracting the residual tar with ether. Physical constants by three different authors are listed in Table II.

(b) To a solution of 7.6 g. of sodium in 120 ml. of absolute alcohol was added 54 g. of carbethoxy-cyclopentanone in twenty minutes at 20°C with efficient stirring. Sixty-four grams of ethyl α-bromopropionate was added to the mixture and refluxed for four hours. A clear red solution resulted. Fifty milliliters of alcohol was distilled off from it and the residue was diluted with 250 ml. of ice water and extracted with ether. The ether solution, after washing with water, dried with sodium sulfate and the ether was evaporated and the residue vacuum-distilled. Fifty and a half grams of fraction boiling 126.5～130°C/2.5 mm. was obtained. Yield, 60%.

2-α-Carboxyethyl-cyclopentanone and Hexane-tricarboxylic Acid-1, 4, 5.—Hydrolysis was effected in the same way as in a) by using 47.5 g. of ketodiester b. p. 126.5～130°C/2.5 mm. and 105 ml. of concentrated hydrochloric acid. On evaporation of ether and redissolving the residue in a small amount of dry ether, 850 mg. of colorless crystals which were difficult to solve in ether, separated, which on crystallization from ethyl acetate-petroleum ether melted at 147°C. Analysis and titration conformed to hexane-tricarboxylic acid-1, 4, 5.

Anal. Found: C, 49.40; H, 6.71. Calcd. for $C_9H_{14}O_6$: C, 49.54; H, 6.47%. Titration. 9.00 mg. required 12.4 ml. of 0.010 N sodium hydroxide. Calcd. for $C_6H_{11}(COOH)_3$: 12.4 ml. From the ether solution after distillation in vacuum was obtained 14 g. of 2-α-carboxyethyl-cyclopentanone b. p. 119～120°C/0.4 mm. Yield, 46%.

2-α-Carbethoxyethyl-cyclopentanone. — Seven grams of 2-α-carboxyethyl-cyclopentanone was dissolved in 20 ml. of absolute alcohol containing 0.7 ml. of concentrated sulfuric acid and refluxed for six hours in a water bath. Twelve milliliters of ethanol was distilled off from the reaction mixture and the residue was poured into 120 ml. of ice water.

The product was extracted with ether and the ether solution was washed with 5% aqueous sodium carbonate solution and with water successively, and dried with sodium sulfate. Evaporation of ether and vacuum-distillation of the residue produced 5.8 g. of 2-α-carbethoxyethyl-cyclopentanone b. p. 93.5～94°C/3 mm. Yield, 70%. λ_{max} 214 mμ log ε 2.02, 288 mμ log ε 1.36; ν_{max} 5.80 μ (C=O).

Anal. Found: C, 64.91; H, 9.21. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

***cis*-Lactone, *trans*-2-α-Carboxyethyl-cyclopentanol and *trans*-Lactone.**—The aqueous sodium hydroxide solution (4.2 g. of sodium hydroxide in 94 ml. of water) of 14.4 g. of 2-α-carboxyethyl-cyclopentanone was gradually (in one hour) added to a solution of 2.3 g. of sodium borohydride in 35 ml. water. The mixture was well shaken after each addition and left to stand for two days at room temperature after the addition was over. It was cooled in an ice bath, and 50 ml. of concentrated hydrochloric acid was added to it with stirring. After the addition was over, it was warmed on a water bath for fifteen minutes, cooled in an ice bath and extracted three times with benzene followed by four times with ether. The combined benzene solution after washing three times with water was dried with sodium sulfate. Benzene was evaporated under reduced pressure and the residue vacuum-distilled. Four and four-fifth grams of *cis*-lactone (3.8 g. of fraction b. p. 73～74°C/2 mm., 1 g. of fraction b. p. 71～72.5°C/2 mm.) was obtained. The latter fraction was also used for further work. Yield, 37%. λ_{max} 215 mμ log ε 1.65; ν_{max} 5.70 μ (C=O) 8.44 μ, 8.60 μ (C-O).

Anal. Found: C, 67.96; H, 8.89. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

To the combined ether solution was added 100 ml. of benzene. Ether and moisture were azeotropically distilled. And the residue was vacuum-distilled. *trans*-2-α-Carboxyethyl-cyclopentanol b. p. 125～126°C/0.4 mm., m. p. 58°C, was obtained. λ_{max} 215 mμ log ε 1.93; ν_{max} 5.90 μ (C=O).

Anal. Found: C, 61.37; H, 9.21. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92%.

***trans*-Lactone Prepared from *trans*-2-α-Carboxyethyl-cyclopentanol.** — In the usual pro-

cedure the residue of the ether extract was directly lactonized by heating it at 180~195°C under 30 mm. pressure from thirty minutes to three hours. *trans*-Lactone mixed with water slowly distilled out. But when one drop of concentrated sulfuric acid was added to the hydroxyacid, lactonization was completed in a few minutes. The product was dissolved in benzene, dried with sodium sulfate. Benzene was evaporated and the residue vacuum-distilled. Four and nine-tenths grams of *trans*-lactone b. p. 67°C/2 mm. was obtained. Yield, 38%. λ_{max} 213.5 mμ log ε 1.81; ν_{max} 5.70 μ (C=O) 8.44 μ, 8.60 μ (C-O).

Anal. Found: C, 68.52; H, 8.80. Calcd. for $C_5H_{12}O_2$: C, 68.54; H, 8.63%.

The author is grateful to Mr. H. Kotsuma* for infrared spectra and Mr. M. Shito and Miss S. Indo for the microanalysis.

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Characteristics of Alginic Acid as a Cation Exchanger and its Application to the Separation of Thorium(IV) and Cerium(III) Ions

By Takeo TAKAHASHI and Shingo MIYAKE

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Alginic acid belongs to one of the polyacids with carboxylic groups as the dissociation group. It is generally soluble in water, either neutral or basic, but can maintain a solid state in an acidic salt solution, showing an excellent cation exchange property[1] and although its analytical and industrial applications have also been investigated[2], the characteristics as cation exchanger or situation in cation exchangers have not yet been explained clearly. It is the principle object of the present research to discuss the cation exchange property of alginic acid from the viewpoint of acidity. Alginic acid indicates somewhat stronger acidity in the aqueous solution than acetic acid[3] and polyacrylic acid which is also one of the polycarboxylic acids. From the viewpoint of the acidity, it is expected that the characteristics of alginic acid as cation exchanger would be placed between a strongly acidic and a weakly acidic exchanger. Thus it may be used advantageously for the ion-exchange separation of some multivalent cations, which are separated with difficulty with conventional exchangers, either strongly or weakly acidic. For example, the separation of thorium(IV) and cerium(III) with alginic acid as exchanger was briefly described in the previous communication[4]. The present paper discusses the characteristics of alginic acid as cation exchanger and the same subject was described in a previous paper in some detail.

Experimental

Alginic acid employed for the measurement of the ion exchange equilibrium was prepared by the following procedure. A commercial sodium alginate was dissolved in water to make about 0.5% solution. The insoluble residue was congelated by warming the solution to 50~60°C on a water bath, and removed by filtering through a filter bed composed of Toyo filter paper No. 2 and No. 5c. Alginic acid, coagulated by the addition of hydrochloric acid to the filtrate, was, after a few hours, collected on a piece of silk gauze of about 60 mesh, and washed with about 50% methanol until the absence of chlorine ions in the washing was confirmed. After the methanol was pressed out, the swelled alginic acid was stored in a closed container with water in the bottom.

Amberlite IR-120, a strongly acidic exchanger and IRC-50, a weakly acidic one were similarly stored in a wet state. Table I shows the properties of these exchangers available for the experiment.

1) J. L. Monger and A. Wassermann, *Nature*, **159**, 746 (1947).
2) H. Specker and H. Hartkamp, *Z. anal. Chem.*, **140**, 167 (1953); **141**, 33 (1954).
3) S. Miyake, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1278 (1958)
4) T. Takahashi and S. Miyake, This Bulletin, **32**, 878 (1959).

TABLE I. THE PROPERTIES OF THE EXCHANGERS

Exchanger	Humidity %	0.1 N NaOH (ml.) for neutralization of 1 g. of exchanger
IR-120	43.1	23.56
H alg.	66.6	18.96
IRC-50	48.5	53.70

The alginic acid used in the column (1.5 cm. in diameter and 20 cm. in length) for the separation of thorium (IV) and cerium (III) ions was prepared from calcium alginate thread* by the procedure described in the previous paper[4].

Other reagents were all of the special grade (G. R.) available commercially.

Spectrophotometric methods were used for the analysis of thorium(IV) and cerium(III) ions, using Neo-thorone for thorium(IV) (580 mμ) and hydrogen peroxide for cerium(III) (320 mμ).

Results and Discussion

Characteristics of Alginic Acid as an Exchanger.—*Apparent dissociation constant.*—IR-120 (0.22 g.), IRC-50 (0.10 g.) and alginic acid (0.28 g.) weighed exactly within a deviation of 1 mg. were immersed in 10 ml. of the mixed solution containing $(10-x)$ ml. of 1 N potassium chloride and x ml. of potassium chloride and potassium hydroxide mixture (1 N KCl–0.1 N KOH), respectively. After the ion exchange equilibrium was achieved by allowing the mixed solution to stand for 24 hr. (for 3 days in the case of IRC-50) with occasional agitation, the pH of each supernatant solution was measured by means of Toa Denpa Model HM-3 glass electrode pH meter. Fig. 1 shows the relationship between the pH of the supernatant solution in its equilibrium state and the volume of 0.1 N potassium hydroxide added.

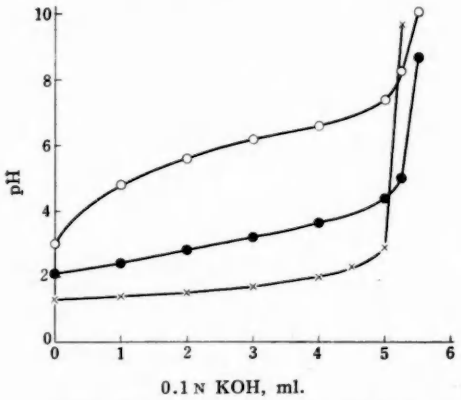

Fig. 1. Titration curves of exchangers.
○: IRC-50, ●: H alg., ×: IR-120

Such curves as those shown in Fig. 1 correspond to the titration curves of the exchangers as polyacids, and have been used for a mean in the characterization of the dissociation group of ion exchangers. For the purpose of expressing the apparent dissociation constant, pK, in the case of a weak polyacid, it is useful to take the value of pH at which half of the polyacid is exactly neutralized.

From Fig. 1, the values of pK for the exchangers are found to be 1.6 for IR-120, 3.1 for alginic acid and 6.0 for IRC-50. Now, attention must be paid to the fact that the values of pH cited above are of the external solution with which the exchangers are in equilibrium, and the true pH[5] in the internal body of the exchangers may show lower values. However, it is concluded that alginic acid is situated between the strongly acidic and the weakly acidic exchangers from the viewpoint of acidity. In fact, it is well known that alginic acid is one of the strongest acids among all the weak polyacids with the carboxylic group. The most valuable characteristic of alginic acid is that it has an intermediate acidity as cation exchanger.

On the other hand, in a cation exchange reaction under a given condition, the difference between the selectivity of different cations is independent in principle of the kind of functional group of exchangers, with the exception of some special exchangers, but the effect of the kind of functional group upon the property of the exchanger is due to the difference of their acidities. When the exchangers have the same functional group and different acidities, a difference in property as ion exchanger should be found. Accordingly, it is expected that alginic acid would have an intermediate property for cations, and that it may be available for the separation of several cations, which are separated with difficulty by means of conventional exchangers.

Distribution constant of thorium(IV) and cerium(III) ions.—Each exchanger, weighed in the same manner as that described above, is immersed in 20 ml. of 3.8×10^{-3} M thorium nitrate solution or 7.1×10^{-3} M cerous nitrate solution, with nitric acid of various concentrations. After equilibrium is reached through the same procedure as

* The alginate thread was supplied from Kamogawa Kato Co., Ltd., to whom the authors are indebted and to whom they express their thanks.

5) M. Honda, *J. Am. Chem. Soc.*, **73**, 2943 (1951).

that described above, thorium(IV) or cerium(III) ions in an aliquot of the supernatant solution were determined.

The distribution constant, K_d, for thorium(IV) and cerium(III) ions in regard to each exchanger was calculated from the following equation.

$$K_d = \frac{\text{Concn. of cation in the exchanger (dry base) (mg./g.)}}{\text{Concn. of cation in the supernatant soln. (mg./ml.)}}$$

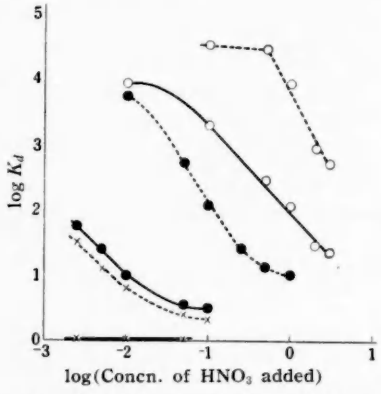

Fig. 2. Effect of concentration of nitric acid upon K_d of thorium(IV) and cerium(III).
------: Th, ——: Ce
○: IR-120, ●: H alg., ×: IRC-50

Fig. 2 shows the relationship between $\log K_d$ and logarithm of concentration of nitric acid in the solution. Now, for the concentrations of nitric acid, the stoichiometrical concentrations in the initial periods of the reaction were used instead of pH at the equilibrium, because of the difficulty of the measurement of pH in a concentrated nitric acid.

It is clear that IRC-50 adsorbs these cations little or not at all from an acid solution which keeps them without hydrolysis, and that these cations are adsorbed by IR-120 too tightly to be eluted fractionally with a dilute solution of conventional mineral acid. The values of K_d for thorium(IV) and cerium(III) ions in regard to alginic acid is placed between those in regard to IR-120 and IRC-50.

For the separation of thorium(IV) and cerium(III) ions by cation exchanger, it has been, heretofore, usual to use strongly acidic exchangers such as Amberlite IR-120 or Dowex-50 and to use complex reagents such as EDTA[6,7], citrate[8] and oxalate[9] for the fractional elution. This is because of the difficulty with which these cations are eluted from strongly acidic exchangers with a dilute acid solution. On the other hand, it is not always easy to convert the complex ions into simple metallic ions. However, it seems likely that thorium(IV) and cerium(III) ions can be easily eluted fractionally with a conventional mineral acid as shown in Fig. 2, provided that alginic acid is used as exchanger. It has never been suggested that an intermediately acidic exchanger such as alginic acid be used for the separation of thorium(IV) and cerium(III) ions.

Separation of Thorium(IV) and Cerium(III) Ions by the Use of Alginic Acid Column.—*Synthetic solution.*—The synthetic solutions containing thorium(IV) and cerium(III) ions in various concentrations were made pH 2 to 2.5 with aqueous ammonia and poured over the top of the column. Thorium(IV) and cerium(III) ions are adsorbed on alginic acid. After the column is washed with 100 ml. of water, cerium(III) ion is eluted with nitric acid of a concentration below 0.1 N at a flow rate of about 1 ml./min., and then the thorium(IV) ion is eluted with 1 N nitric acid. An example of the elution diagram has been shown in the previous paper[4]. Some analytical results are given in Table II.

TABLE II. SEPARATION OF THORIUM(IV) AND CERIUM(III) IONS FROM THEIR SYNTHETIC SOLUTION

Taken mg.		Found mg.		Concn. and vol. of eluted soln. for Ce		for Th	
Th	Ce	Th	Ce	N	ml.	N	ml.
35.5	30.0	35.5	30.1	0.05	250	1	100
35.5	30.0	35.4	30.3	0.075	200	〃	〃
70.0	30.0	69.9	30.0	〃	〃	〃	150
35.5	45.0	35.5	44.8	0.1	〃	〃	100
70.0	45.0	70.1	44.9	〃	〃	〃	150
70.0	60.0	70.0	47.4	〃	300	〃	〃
105.5	45.0	105.7	45.0	〃	200	〃	〃

It is shown that the present method can be feasible for the quantitative separation of thorium(IV) and cerium(III) ions and that the column employed in this experiment has a dimension suitable for the adsorption of the cerium(III) ion below 45 mg.

6) L. Gordon et al., *Anal. Chem.*, **28**, 1476 (1956).
7) T. Taketatsu, This Bulletin, **32**, 291 (1959).
8) T. Nishi et al., *III Atomic Energy Symposium, Japan*, 69 (1959).
9) T. Nozaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 996 (1955).

Application to monazite. — The monazite employed in this experiment was mined in 1940 at Ishikawa-yama, Fukushima-ken. Monazite ore was digested with concentrated sulfuric acid in the usual way. Mixed oxalates of thorium(IV) and rare earth metals were separated from other metallic ions through reprecipitation with oxalic acid. The oxalate mixture was converted into hydroxide by immersing into a warm sodium hydroxide solution and then dissolved in nitric acid. After the ceric ion contained in the mixed solution was reduced with a small amount of sodium nitrite to the cerous ion, and after the pH was adjusted with nitric acid to about 1, an aliquot of the solution was poured over the top of the column, which then was washed with 250 ml. of 0.1 N nitric acid at a flow rate of about 1 ml./min. Thus, the thorium(IV) ion is adsorbed entirely on alginic acid in the column, while all rare earth metal ions pass through the column. The results are shown in Table III.

TABLE III. SEPARATION OF THORIUM(IV) AND RARE EARTH IONS FROM MONAZITE

Mixed oxide	ThO_2 found in the column	Oxides of R.E. found in the effluent	Other oxides eluted with 1 N H_2SO_4
mg.	mg.	mg.	mg.
298	42.5	237.1	18.3
〃	42.8	237.3	17.8
〃	43.1	236.8	19.1

The "other oxides" shown in the last column of Table III are the oxides not eluted with 1 N nitric acid but eluted with 1 N sulfric acid. They seem to be composed of the oxides of titanium, zirconium and hafnium. In this experiment, the mixed oxide, the oxides of rare earth elements and "other oxides" were precipitated with aqueous ammonia from respective solutions and determined gravimetrically.

Summary

The apparent dissociation constant of alginic acid was measured by means of the neutralization with 0.1 N potassium hydroxide in 1 N potassium chloride solution and found to have a value of 3.1. This value is between that of IR-120 and of IRC-50, which is obtained by the same manner of measurement. The values of K_d for thorium(IV) and cerium(III) ions in regard to these three exchangers were measured, showing that the value in regard to alginic acid is also situated between the other two.

The application of alginic acid to the fractional separation of thorium(IV) and cerium(III) ions gave a satisfactory result.

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*Studies on 3-(Anthraquinon-1-yl)oxazolidin-2-ones. II. 3-(Bromoanthraquinon-1-yl)oxazolidin-2-ones and their Related Compounds**

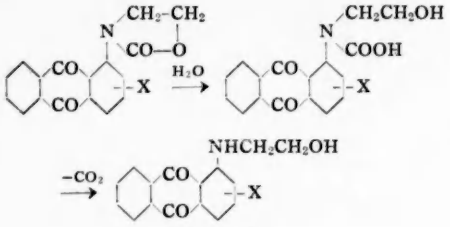
By Kō Naiki

(Recieved June 10, 1959)

It was shown in a previous paper[1] that an introduction of a methyl group into an anthraquinone nucleus of 3-(anthraquinon-1-yl)oxazolidin-2-one decreases the reactivity with an aqueous solution of potassium hydroxide. In other words, the existence of a steric hindrance of the 2-methyl group plays an important part in the hydrolysis process (Scheme I), inhibiting the conversion of the anthraquinon-1-yl-oxazolidin-2-ones into the 1-*N*-2-hydroxyethylaminoanthraquinones to a certain extent.

* Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

1) K. Naiki, This Bulletin, **32**, 361 (1959).



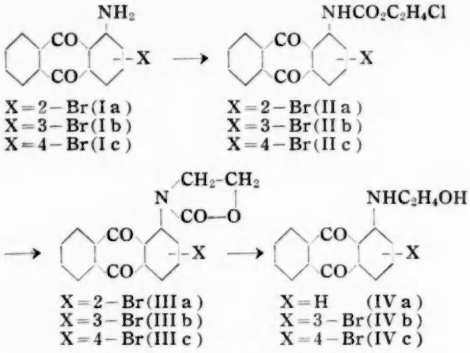
Scheme I

Furthermore, it was shown that in the case of the spectra of 2-chloroethyl methylanthraquinon-1-ylcarbamates the steric inhibition of the $\pi-p$ conjugation, i.e. interaction between an anthraquinone ring and an unshared electron pair of the nitrogen atom, plays an important role. Thus the introduction of the 2-methyl group into the anthraquinone ring results in the lowering of the intensity of the band near 400 mμ ascribed to the Aq-$\ddot{N}$ chromophore, where Aq represents the anthraquinone ring, and results in the displacement by 43 mμ towards shorter wavelength as compared with 2-chloroethyl 4-methylanthraquinon-1-ylcarbamate. In 3-(methylanthraquinon-1-yl) oxazolidin-2-ones, the steric inhibition of the $\pi-p$ conjugation due to a bulky *N*-substituent, oxazolidin-2-onyl, results in the lowering of the intensity of the band near 400 mμ to a greater extent, and the introduction of the 2-methyl group into the anthraquinone ring weakens the band associated with Aq-$\ddot{N}$ chromophore.

In the present study, 3-(bromoanthraquinon-1-yl)oxazolidin-2-ones, 2-chloroethyl bromoanthraquinon-1-ylcarbamates and 1-*N*-2-hydroxyethylamino-bromoanthraquinones were synthesized and the effect of the bromine atom according to its position on absorption spectra of 2-chloroethyl bromoanthraquinon-1-ylcarbamates and 3-(bromoanthraquinon-1-yl) oxazolidin-2-ones was discussed in terms of the steric hindrance. None of them has yet been prepared. Furthermore, the effect of the bromine atom according to its position on the reactivity of bromoanthraquinon-1-yloxazolidin-2-ones with potassium hydroxide was investigated.

Preparation and Results

The syntheses of the compounds were carried out according to the following processes (Scheme II).



Scheme II

2-Chloroethyl 2-bromoanthraquinon-1-ylcarbamate(IIa), 3-bromoanthraquinon-1-ylcarbamate(IIb) and 4-bromoanthraquinon-1-ylcarbamate(IIc) were obtained from the corresponding 1-amino-bromoanthraquinones (Ia, Ib and Ic, respectively) by the action of 2-chloroethyl chloroformate in the presence of sodium carbonate in boiling xylene.

3-(2-Bromoanthraquinon-1-yl)oxazolidin-2-one(IIIa) was prepared from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate by the action of a 20% aqueous solution of potassium hydroxide at 98~99°C for 1 hr. The mixture of 1-*N*-2-hydroxyethylaminoanthraquinone(IVa) and 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one(IIIa) was obtained from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate by the action of a 20% aqueous solution of potassium hydroxide at 105~107°C for 1 hr. Each of the constituents was separated by a column chromatography from benzene on alumina.

The mixture of 1-*N*-2-hydroxyethylamino-3-bromoanthraquinone(IVb), 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one(IIIb) and 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate was obtained from 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate by the action of a 20% aqueous solution of potassium hydroxide at 98~99°C for 1 hr. and each of the constituents was separated by a column chromatography from benzene on alumina. In the same way, 1-*N*-2-hydroxyethylamino-4-bromoanthraquinone(IVc) and 3-(4-bromoanthraquinon-1-yl)oxazolidin-2-one(IIIc) were obtained from 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate.

The proportion of constituents of the reaction mixture from the corresponding 2-chloroethyl bromoanthraquinon-1-ylcarbamates by the action of a 20% aqueous

TABLE I. THE PROPORTIONS OF THE CONSTITUENTS OF THE REACTION PRODUCTS OBTAINED FROM 2-CHLOROETHYL BROMOANTHRAQUINON-1-YLCARBAMATES AND A 20% AQUEOUS SOLUTION OF POTASSIUM HYDROXIDE

Position of Br	II %	III %	IV %
2	0	100	0
3	29	7	64
4	44	26	30

solution of potassium hydroxide at 98~99°C for 1 hr. was determined.

The results are shown in Table I. The reaction mixture obtained from the chloroethyl bromoanthraquinon-1-ylcarbamate and potassium hydroxide can be separated into the constituents by a column chromatography from benzene on alumina, but it is observed that the 2-chloroethyl bromoanthraquinon-1-ylcarbamate is gradually converted into the corresponding bromoanthraquinon-1-yloxazolidin-2-one on alumina. For this reason, the determination of the proportion of constituents was carried out by a spectrophotometry. Since the absorption bands of the constituents are separated from each other, the determination was carried out exactly. The absorption spectra of 2-chloroethyl bromoanthraquinon-1-ylcarbamates, 3-(bromoanthraquinon-1-yl)oxazolidin-2-ones and 1-*N*-2-hydroxyethylamino-bromoanthraquinones are shown in Figs. 1—3, respectively.

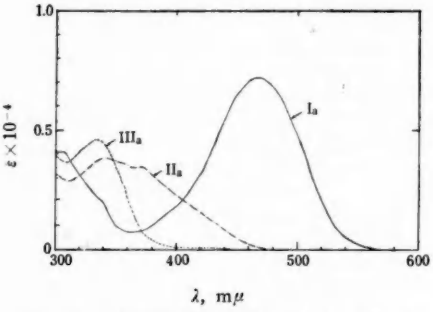


Fig. 1. Absorption spectra of 1-amino-2-bromoanthraquinones.
Ia: 1-Amino-2-bromoanthraquinone (in ethanol)
IIa: 2-Chloroethyl 2-bromoanthraquinon-1-ylcarbamate (in toluene)
IIIa: 3-(2-Bromoanthraquinon-1-yl)-oxazolidin-2-one (in toluene)

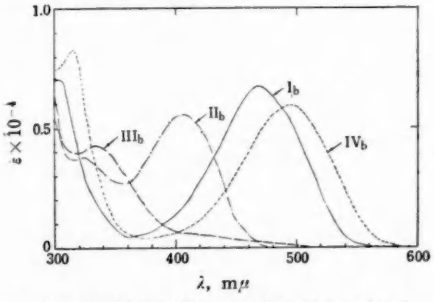


Fig. 2. Absorption spectra of 1-amino-3-bromoanthraquinones.
Ib: 1-Amino-3-bromoanthraquinone (in ethanol)
IIb: 2-Chloroethyl 3-bromoanthraquinon-1-ylcarbamate (in toluene)
IIIb: 3-(3-Bromoanthraquinon-1-yl)-oxazolidin-2-one (in toluene)
IVb: 1-*N*-2-Hydroxyethylamino-3-bromoanthraquinone (in toluene)

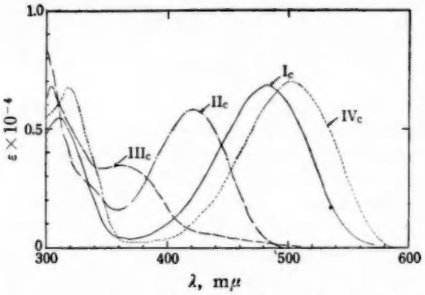


Fig. 3. Absorption spectra of 1-amino-4-bromoanthraquinones.
Ic: 1-Amino-4-bromoanthraquinone (in ethanol)
IIc: 2-Chloroethyl 4-bromoanthraquinon-1-ylcarbamate (in toluene)
IIIc: 3-(4-Bromoanthraquinon-1-yl)-oxazolidin-2-one (in toluene)
IVc: 1-*N*-2-Hydroxyethylamino-4-bromoanthraquinone (in toluene)

TABLE II. ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF 1-AMINO-BROMOANTHRAQUINONES

Compound	λ_{max}, mμ		$\varepsilon_{max} \times 10^{-4}$	
I a*	308	469	0.436	0.760
I b*	~305	471	(0.732)	0.689
I c*	312	483	0.570	0.701
II a**	342	370	0.386	0.346
II b**	325	406	0.375	0.555
II c**	~335	423	(0.269)	0.580
III a**	334	~395	0.472	(0.031)***
III b**	335	~410	0.417	(0.062)***
III c**	342	~420	0.347	(0.064)***
IV b**	313	496	0.821	0.593
IV c**	318	503	0.683	0.697

Bracketed values are absorption bands of low intensity.
* Solvent: ethanol; concn. 1×10^{-4} mol./l.
** Solvent: toluene; concn. 1×10^{-4} mol./l.
*** Solvent: toluene; concn. 1×10^{-3} mol./l.

Absorption maxima and extinction coefficients are given in Table II.

Discussion

Effect of the Bromine Atom according to its Position on Absorption Spectra.—In the case of the spectra of 2-chloroethyl anthraquinon-1-ylcarbamates, the introduction of the 2-bromine atom into an anthraquinone ring results in the lowering of an intensity of the band near 400 mμ ascribed to Aq-N̈ chromophore and the displacement by 53 mμ towards a shorter wavelength as compared with 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate. This fact may be explicable in terms of the steric hindrance of the $\pi-p$ conjugation, between the anthraquinone ring and an unshared electron pair of the nitrogen atom, due to a repulsion between the carbonyl group and the 2-bromine atom which arises from the overlapping of the van der Waals radii. It is pointed out that $\varepsilon_2/\varepsilon_4$ is considerably smaller for 2-chloroethyl bromoanthraquinon-1-ylcarbamates than for 2-chloroethyl methylanthraquinon-1-ylcarbamates. Projection diagrams (Fig. 4) of uniplanar

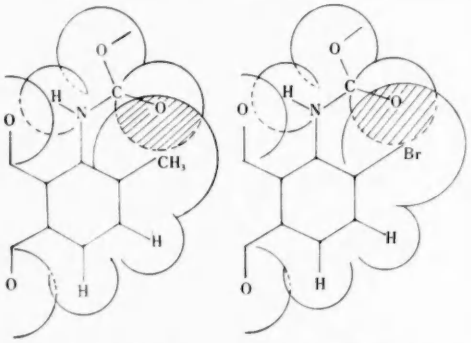


Fig. 4. Projection diagrams of 2-chloroethyl 2-bromo- and 2-methyl-anthraquinon-1-yl-carbamates.

structures, employing van der Waals radii, indicate only a slightly larger overlapping for 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate than for 2-chloroethyl 2-methylanthraquinon-1-ylcarbamate. Hence additional effects, i. e. the coulombic interaction of the carbonyl group with the 2-bromine atom and the hydrogen bonding between the carbonyl group and the 2-methyl group, must be considered in an explanation of the spectral diffrence between 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate and 2-methylanthraquinon-1-ylcarbamate (Table III).

TABLE III. ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF THE PRIMARY BANDS OF 2-CHLOROETHYL ANTHRAQUINON-1-YLCARBAMATES

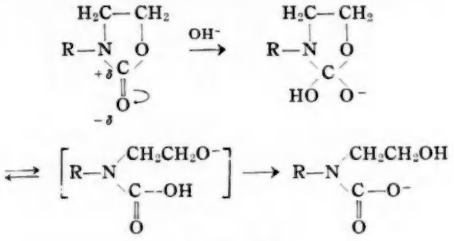
Substituent of anthraquinone nucleus	λ_{max} mμ	$\varepsilon\times10^{-4}$	$\varepsilon_2/\varepsilon_4$
2-Methyl	378	0.520(ε_2)	0.84
4-Methyl	421	0.618(ε_4)	
2-Bromo	370	0.346(ε_2)	0.60
4-Bromo	423	0.580(ε_4)	

In the spectra of 3-(anthraquinon-1-yl)-oxazolidin-2-ones, it is expected that an absence of intermolecular hydrogen bonding possibility results in the lowering of the intensity of the band near 400 mμ as compared with the compounds which have intermolecular hydrogen bonding possibility, 2-chloroethyl anthraquinon-1-ylcarbamates. It is further expected that the introduction of a bulky group, such as oxazolin-2-onyl, into the 1-position of the anthraquinone ring increases the extent of steric inhibition of the $\pi-p$ conjugation, between the anthraquinone ring and the unshared electron pair of the nitrogen atom, and results in the lowering of the intensity of the band near 400 mμ ascribed to Aq-N̈ chromophore. If the 2-bromine atom is introduced into the anthraquinone ring, the steric hindrance inhibits the $\pi-p$ conjugation between the ring and the unshared electron pair of the nitrogen atom to a greater extent. This is illustrated in Table II.

The Effect of the 2-Bromine Atom on the Reactivity of 3-(Bromoanthraquinon-1-yl)-oxazolidin-2-ones with the Hydroxide Ion.—On account of an aqueous dispersion of solid material, various difficulties may be introduced in the discussion when the reactivities are compared with each other. Nevertheless, it may be probable that some close relation exists between the reactivity and factors such as electronic and steric effects of groups in the anthraquinone nucleus. Table I shows clearly that the 2-bromine atom decreases the reactivity of the 3-(bromoanthraquinon-1-yl)-oxazolidin-2-ones with potassium hydroxide to a considerable extent. In other words, it shows the existence of a steric hindrance of the 2-bromine atom in the hydrolysis, this effect inhibiting the conversion of 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one into 1-*N*-2-hydroxyethylamino-2-bromoanthraquinone.

In the basic hydrolysis of 3-substituted oxazolidin-2-ones, there is a carbonyl carbon atom at which attack would be

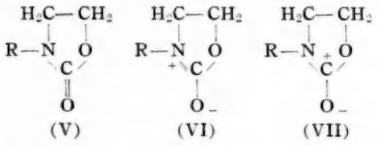
expected to occur. A mechanism of the hydrolysis reaction may be illustrated as follows (Scheme III).



Scheme III

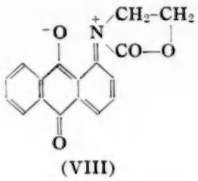
The addition complex has a more or less tetrahedral configuration at the site of substitution. Its formation controls the rate of the reaction. It may be probable, therefore, that the steric hindrance to the formation of the addition complex, due to overlapping of the van der Waals radii and the coulombic interaction of the 2-bromine atom with the hydroxide ion, inhibits the conversion of 3-(2-bromoanthraquinon-1-yl)-oxazolidin-2-one into 1-*N*-2-hydroxyethyl-amino-2-bromoanthraquinone. Further effects must, however, be considered in an explanation of the experimental results.

3-Substituted oxazolidin-2-ones may be described as a resonance hybrid of structures V—VII.



(V) (VI) (VII)

If the –N̈–C=O system is planar, there will be a flow of a charge away from the nitrogen atom into the carbonyl oxygen atom; in other words, structure VI is much more important than structure VII, in which the positive charge is on the carbonyl carbon atom. In 3-anthraquinon-1-yloxazolidin-2-ones, an additional structure VIII contributes to the resonance hybrid. This means that if the Aq–N̈ system is planar, there will be a flow of a charge away from the nitrogen atom into the anthraquinone ring, this resulting in a decrease of the contribution of structure VI to the resonance hybrid. The steric hindrance of the 2-bromine atom to the planar configuration of the Aq–N̈ system decreases the contribution of structure VIII, increasing the contribution of structure VI to the resonance hybrid.



(VIII)

On the other hand, a nucleophilic attack occurs readily at the position at which an open sextet of electrons can be provided readily. It is therefore reasonable to suppose that the contribution of structure VI is unfavorable for the formation of an addition complex in the reaction of 3-(anthraquinon-1-yl)oxazolidin-2-ones with the hydroxide ion. The steric hindrance of the 2-bromine atom to the planar configuration of the Aq–N̈ system inhibits the conversion of 3-(2-bromoantraquinon-1-yl)-oxazolidin-2-one into 1-*N*-2-hydroxyethyl-amino-2-bromoanthraquinone.

It is also expected that the introduction of electron attracting groups into the anthraquinone ring results in the decrease of contribution of strueture VI to the resonance hybrid and the formation of the addition complex will be facilitated, increasing the rate of conversion of 3-(anthraquinon-1-yl)oxazolidin-2-ones into 1-*N*-2-hydroxyethylaminoanthraquinones. This is illustrated by the comparison of reactivities of 3-(bromoanthraquinon-1-yl)-oxazolidin-2-ones with those of 3-(methyl-anthraquinon-1-yl)oxazolidin-2-ones (Table IV).

TABLE IV. CONVERSION OF 3-(ANTHRAQUINON-1-YL)OXAZOLIDIN-2-ONES INTO 1-*N*-2-HYDROXY-ETHYLAMINOANTHRAQUINONES*

Compound	Conversion, %
3-(2-Methylanthraquinon-1-yl)oxazolidin-2-one	17
3-(2-Bromoanthraquinon-1-yl)oxazolidin-2-one	0
3-(3-Methylanthraquinon-1-yl)oxazolidin-2-one	73
3-(3-Bromoanthraquinon-1-yl)oxazolidin-2-one	90
3-(4-Methylanthraquinon-1-yl)oxazolidin-2-one	41
3-(4-Bromoanthraquinon-1-yl)oxazolidin-2-one	54

* KOH, 20%; Temp., 98~99°C; Reaction time, 1 hr.

Experimental

1-Amino-2-bromoanthraquinone (Ia).—Red plates (glacial acetic acid), m. p. 179~180°C.

Anal. Found: N, 4.62. Calcd. for $C_{14}H_8O_2NBr$: N, 4.64%.

1-Amino-3-bromoanthraquinone (Ib)[2]. — Red prisms (glacial acetic acid), m. p. 242~243°C.

Anal. Found: N, 4.70. Calcd. for $C_{14}H_8O_2NBr$: N, 4.64%.

2) F. Ullmann and O. Fisher, *Ber.*, **49**, 2154 (1956).

1-Amino-4-bromoanthraquinone (Ic)[3].—The compound was separated by a column chromatography from benzene on alumina and recrystallized from ligroin, giving red needles, m. p. 179~180°C.

Anal. Found: N, 4.69. Calcd. for $C_{14}H_8O_2NBr$: N, 4.64%.

2-Chloroethyl 2-Bromoanthraquinon-1-ylcarbamate (IIa)[4].—Yellow needles (ethyl alcohol), m. p. 188~189°C.

Anal. Found: N, 3.48. Calcd. for $C_{17}H_{11}O_4NBrCl$: N, 3.42%.

2-Chloroethyl 3-Bromoanthraquinon-1-ylcarbamate (IIb).—A mixture of 2.00 g. of 1-amino-3-bromoanthraquinone (m. p. 240~241°C), 1.20 g. of 2-chloroethyl chloroformate (b. p. 150~151°C), 0.90 g. of sodium carbonate and 30 ml. of xylene was refluxed with stirring for 8 hr. The insoluble material was removed by hot filtration and the filtrate was evaporated to a volume of about 15 ml. for crystallization. Yield, 2.65 g. (99% of the theory) of yellow needles, m. p. 215~216°C. It was recrystallized from ethanol, giving yellow needles, m. p. 220~221°C.

Anal. Found: N, 3.53. Calcd. for $C_{17}H_{11}O_4NBrCl$: N, 3.42%.

2-Chloroethyl 4-Bromoanthraquinon-1-ylcarbamate (IIc).—A mixture of 2.00 g. of 1-amino-4-bromoanthraquinone (m. p. 175~176°C) 1.20 g. of 2-chloroethyl chloroformate (b. p. 150~151°C), 0.90 g. of sodium carbonate and 20 ml. of xylene was refluxed with stirring for 2 hr. The insoluble material was removed by hot filtration and the filtrate was evaporated to a volume of about 10 ml. for crystallization. Yield, 2.55 g. (94% of the theory) of yellow needles, m. p. 201~202°C. It was recrystallized from ethanol, giving yellow needles, m. p. 203~204°C.

Anal. Found: N, 3.67. Calcd. for $C_{17}H_{11}O_4NBrCl$: N, 3.42%.

3-(2-Bromoanthraquinon-1-yl)oxazolidin-2-one (IIIa)[4].—Pale brown plates (toluene), m. p. 284°C (decomp.).

Anal. Found: N, 4.09. Calcd. for $C_{17}H_{10}O_4NBr$: N, 4.11%.

3-(3-Bromoanthraquinon-1-yl)oxazolidin-2-one (IIIb) and 1-*N*-2-Hydroxyethylamino-3-bromoanthraquinone (IVb).—A mixture of 1.00 g. of finely powdered 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate and 30 g. of a 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hr. After being diluted with water, the precipitate was collected, washed with water, and dried. Yield, 0.92 g. of reddish brown powder. The product, consisting of 1-*N*-2-hydroxyethylamino-3-bromoanthraquinone, 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one and 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate, was dissolved in benzene and chromatographed on alumina. 1-*N*-2-Hydroxyethylamino-3-bromoanthraquinone is most strongly adsorbed and 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one is more strongly adsorbed than 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate, which is gradually converted into 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one on alumina in the column. The red band, containing 1-*N*-2-hydroxylamino-3-bromoanthraquinone, was eluted by the use of ethanol. Yield, 0.15 g. of red needles, m. p. 213~214°C. It was recrystallized from toluene, giving red needles, m. p. 213~214°C.

Anal. Found: N, 4.08. Calcd. for $C_{16}H_{12}O_3NBr$: N, 4.11%.

The pale brown band, containing 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.07 g. of pale brown crystalline powder, m. p. 215~229°C. It was recrystallized from ethanol, giving pale brown needles, m. p. 243~244°C.

Anal. Found: N, 3.73. Calcd. for $C_{17}H_{10}O_4NBr$: N, 3.76%.

The yellow elute, containing 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate, was evaporated for crystallization. Yield, 0.70 g. of yellow needles, m. p. 212~215°C.

3-(4-Bromoanthraquinon-1-yl)oxazolidin-2-one (IIIc) and 1-*N*-2-Hydroxyethylamino-4-bromoanthraquinone (IVc).—A mixture of 1.00 g. of finely powdered 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate (m. p. 201~202°C) and 30 g. of a 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hr. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.88 g. of reddish brown powder. The product was treated as in the foregoing experiment. The red band, containing 1-*N*-2-hydroxyethylamino-4-bromoanthraquinone, was eluted by the use of ethanol. Yield, 0.45 g. of red needles, m. p. 176~177°C. It was recrystallized from ethanol, giving red needles, m. p. 181~182°C.

Anal. Found: N, 4.09. Calcd. for $C_{16}H_{12}O_3NBr$: N, 4.11%.

The pale brown band, containing 3-(4-bromoanthraquinon-1-yl)oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.20 g. of pale brown needles, m. p. 197~202°C. It was recrystallized from ethanol, giving pale brown needles, m. p. 208~209°C.

Anal. Found: N, 3.98. Calcd. for $C_{17}H_{10}O_4NBr$: N, 3.76%.

The yellow elute, containing 2-chloroethyl 4-bromoanthraquinon-1-yl-carbamate, was evaporated for crystallization. Yield, 0.10 g. of yellow needles, m. p. 184~190°C.

1-*N*-2-Hydroxyethylaminoanthraquinone (IVa).—A mixture of 0.50 g. of 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate (m. p. 191~192°C) and 15 g. of a 20% aqueous solution of potassium hydroxide was refluxed with vigorous stirring for 1 hr. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.40 g. of brownish red powder. It was treated as in the foregoing experiment. The red band, containing 1-*N*-2-hydroxyethylaminoanthraquinone, was eluted by the use of ethanol. Yield, 0.05 g. of red needles, m. p. 169~171°C. A mixed m. p. with authentic 1-*N*-2-hydroxyethylaminoanthraquinone[5] (m.p. 172°C) was 170~171°C.

3) Ger. Pat., 266,563 (1913).

4) K. Naiki, *J. Soc. Org. Syn. Chem., Japan* (*Yūki Gōsei Kagaku Kyōkaishi*), **14**, 84 (1954).

5) K. Naiki, ibid., **12**, 401 (1954).

The pale brown band, containing 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.30 g. of pale brown plates, m. p. 265°C (decomp.).

Determination of the Proportion of the Constituents of the Reaction Product Obtained from 2-Chloroethyl Bromoanthraquinon-1-ylcarbamate and a 20% Aqueous Solution of Potassium Hydroxide.—A mixture of 0.20 g. of finely powdered 2-chloroethyl bromoanthraquinon-1-ylcarbamate and 6.0 g. of a 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hr. After being diluted with water, the precipitate was colleted, washed with water and dried. Yield, 0.18 g. of brownish red powder from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate; 0.18 g. of brownish red powder from 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate; 0.18 g. of brownish red powder from 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate. The proportion of the constituents of the products obtained above was determined by a Shimadzu QB-50 electrophotometer. Optical densities (D) of the toluene solution of the products are shown in Tables V—VII. It was found by simple calculation that the reaction product obtained from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate contains 174 mg. of 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one; the product obtained from 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate contains 10 mg. of 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one, 106 mg. of 1-*N*-2-hydroxyethylamino-3-bromoanthraquinone and 57 mg. of 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate; the product obtained from 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate contains 46 mg. of 3-(4-bromoanthraquinon-1-yl)oxazolidin-2-one, 49 mg. of 1-*N*-2-hydroxyethylamino-4-bromoanthraquinone and 86 mg. of 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate.

TABLE V. OPTICAL DENSITIES OF THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 2-BROMOANTHRAQUINON-1-YLCARBAMATE*

λ mμ	D	$\varepsilon \times 10^{-4}$	
		IIa	IIIa
330	0.480	0.370	0.466
370	0.125	0.346	0.124

* Solvent: toluene; concn. 38 mg./l.

TABLE VI. OPTICAL DENSITIES OE THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 3-BROMOANTHRAQUINON-1-YLCARBAMATE*

λ mμ	D	$\varepsilon \times 10^{-4}$		
		IIb	IIIb	IVb
330	0.528	0.372	0.417	0.432
410	0.281	0.556	0.064	0.076
500	0.446	0.020	0.007	0.590

* Solvent: toluene; concn. 43 mg./l.

TABLE VII. OPTICAL DENSITIES OF THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 4-BROMOANTHRAQUINON-1-YLCARBAMATE*

λ mμ	D	$\varepsilon \times 10^{-4}$		
		IIc	IIIc	IVc
340	0.336	0.240	0.347	0.353
420	0.324	0.560	0.054	0.098
500	0.255	0.051	0.007	0.696

* Solvent: toluene; concn. 42 mg./l.

The author is indebted to Mr. Yoshié Tanizaki for his helpful advice, to Mr. Toshirō Iijima for his helpful discussions and also Professor S. Tsuruoka for his encouragement throughout the present study.

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Crystallization-sensitive Band of Polyvinyl Alcohol

By Hiroyuki TADOKORO

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So-called "crystallization-sensitive bands" in the infrared absorption spectra have recently been found with various kinds of high polymers, such as polyethylene[1-5], polyethylene terephthalate[6-8], polychlorotrifluoroethylene[9], rubber hydrochloride[10], neoprene[11], polyamides[12-14], polyethylene glycol[15], polyvinylidene chloride[16], gutta percha[17], etc. Bands of this kind have at present interested many investigators as one of the powerful measures of the degree of crystallinity, or as a useful clue for the elucidation of the fine structure of the crystalline high polymers[12].

As to the 1141 cm^{-1} band in the infrared spectrum of polyvinyl alcohol (PVA), Elliott, Ambrose and Temple[18] reported that this band shows strong dichroism, and Nagai and his coworkers[19] found that this band becomes more and more intense as heat-treatment proceeds, up to the temperature at which the sample becomes colored. In a previous paper[20] they have concluded that degrees of crystallinity determined by density, sorption of water vapor and infrared absorption methods are approximately in linear relationship unless the thermal decomposition is considerable, and that the 1141 cm^{-1} band is recognized as a so-called crystallization-sensitive band. The nature of this band has been discussed by several authors as will be described below, but is still in a stage of speculation. Accordingly it is highly desirable that further new experimental facts should be accumulated. In the present paper the author will report the experimental results obtained on the proposed crystallization-sensitive band of PVA.

Experimental

a) Samples.—Film specimens were prepared by the same procedures as those described in the previous paper[21].

b) Measurements of the Pleochroism.—A doubly oriented specimen was prepared as follows. A uniaxially oriented PVA film* was rolled with a hot roller at about 90°C (to about four times its length compared with the original one) by holding it between two sheets of nylon 610**. In this procedure the direction of rolling was the same as that of stretching. The double orientation of the sample prepared in this way was ascertained by taking an X-ray Sauter photograph.

Fig. 1 shows schematically the relation between the cross-section perpendicular to the direction of rolling (the direction of the molecular chain axis) of the doubly oriented PVA film and the incident polarized infrared radiation***. As is shown in this figure, both the electric vector and the direction of propagation of the polarized infrared beam are perpendicular to the direction of rolling which is normal to the plane of the figure. The infrared spectra were observed at various angles of the incident beam, namely, 0, 45, 60, 70 and 75°. These infrared measurements were carried out by using a Perkin-Elmer Model 21 Infrared Spectrophotometer with AgCl polarizer.

1) R. B. Richards, *J. Appl. Chem.*, **1**, 370 (1951).
2) R. S. Stein and G. B. B. M. Sutherland, *J. Chem. Phys.*, **22**, 1993 (1954); R. S. Stein, ibid., **23**, 734 (1955).
3) A. Keller and I. Sandeman, *J. Polymer Sci.*, **15**, 133 (1955).
4) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).
5) M. C. Tobin, ibid., **23**, 891 (1955).
6) W. H. Cobbs, Jr. and R. L. Burton, *J. Polymer Sci.*, **10**, 275 (1953).
7) R. G. J. Miller and H. A. Willis, ibid., **19**, 485 (1956).
8) A. B. Thompson and D. W. Wood, *Nature*, **176**, 78 (1955).
9) H. Matsuo, *J. Polymer Sci.*, **21**, 331 (1956); This Bulletin, **30**, 593 (1957).
10) P. B. Checkland and W. H. T. Davison, *Trans. Faraday Soc.*, **52**, 151 (1956).
11) W. E. Mochel and M. B. Hall, *J. Am. Chem. Soc.*, **71**, 4082 (1949); J. T. Maynard and W. E. Mochel, *J. Polymer Sci.*, **13**, 235 (1954).
12) J. B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954).
13) I. Sandeman and A. Keller, *J. Polymer Sci.*, **19**, 401 (1956).
14) H. W. Starkweather, Jr. and R. E. Moynihan, ibid., **22**, 363 (1956).
15) W. H. Davison, *J. Chem. Soc.*, **1955**, 3270.
16) R. L. Burton, W. H. Cobbs, Jr. and V. C. Haskell, *J. Polymer Sci.*, **7**, 569 (1951).
17) G. B. B. M. Sutherland and A. V. Jones, *Discussions Faraday Soc.*, **9**, 281 (1950).
18) A. Elliott, E. J. Ambrose and R. B. Temple, *J. Chem. Phys.*, **16**, 877 (1948).
19) E. Nagai, S. Mima, S. Kuribayashi and N. Sagane, *Chem. High Polymers (Kobunshi Kagaku)*, **12**, 199 (1955).
20) H. Tadokoro, S. Seki and I. Nitta, This Bulletin, **28**, 559 (1955).
21) H. Tadokoro, ibid., **32**, 1252 (1959).

* See Ref. 21.

** Kindly supplied by Dr. H. Yumoto of Tôyô Rayon Co., Ltd.

*** It may be noticed that the angle β of the crystal lattice given in the text of Bunn's paper[22] is different from that of the figure. Fig. 1 in the present paper was reproduced according to the text of Bunn's paper.

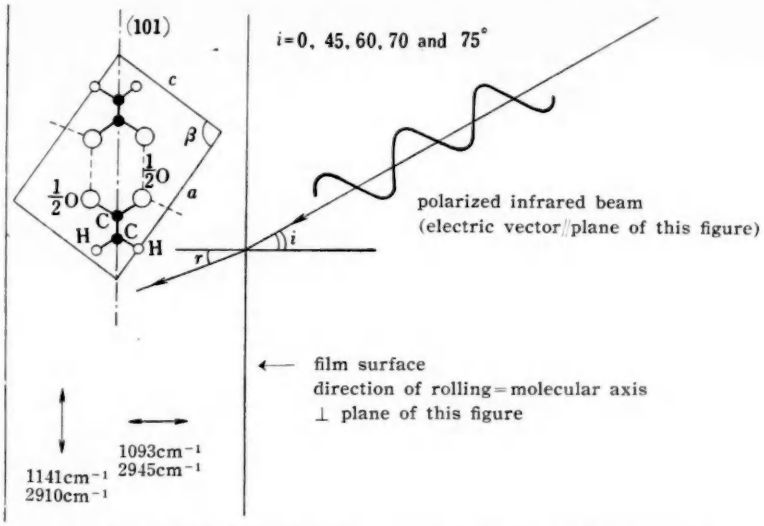

Fig. 1. The relation between the cross-section of the doubly oriented PVA film and the incident polarized infrared beam.

c) Formalization and Swelling in Water.—The PVA samples used for the experiments of formalization and swelling in water, were the same as samples I and III described in the previous papers[20,21]. The details of the experimental condition of the formalization was also given in the previous paper[22]. Those samples were also subjected to swelling in water at room temperature for 2 days. The degrees of swelling for samples I and III in this experimental condition are about 4.7 and 0.7, respectively. The infrared absorption spectra and X-ray diffraction photographs were taken by using a Hilger H800 Infrared Spectrophotometer and an ordinary Laue camera, respectively, before and after the treatment of formalization and swelling in water. During the X-ray measurements the swollen samples were held between aluminum foils in order to prevent the vaporization of water from the samples.

Results and Discussion

a) Pleochroism of the 1141 cm^{-1} Band.—When a polymer is stretched, the crystallites (or molecular chains) are so oriented that the molecular chain axes will be arranged parallel to the stretched direction, but the orientation of the molecular plane in the cross-section perpendicular to the direction of stretching remains completely random. Such a kind of orientation is called a "uniaxial orientation" and the usual fibers have more or less this kind of orientation. When the uniaxially oriented film is rolled in an adequate condition, a certain plane parallel to the molecular axis (in the case of PVA, the plane of carbon zigzag chain) is oriented further parallel to the rolled plane. Such a mode of orientation is called "double orientation". This possibility of double orientation was found for the first time by Bunn et al. on polyethylene[23] and nylon 66[24] by the use of X-ray diffraction, and afterwards this procedure was applied to the infrared studies of nylon 66, PVA and polyethylene by Ambrose and his coworkers[25] in the 3 μ region, and of polyethylene terephthalate by Miller and Willis in the 5~15 μ region[26].

The infrared studies of the doubly oriented PVA sample were carried out in the 3 μ region by Glatt et al.[27] and Elliott et al.[25] By the use of the pleochroism of the CH_2 stretching modes, they found that the plane of the carbon zigzag chain is parallel to the rolled plane of the film.

If the transition moment of an absorption band is perpendicular to the direction of rolling and exists in the rolled plane of

22) C. W. Bunn, *Nature*, **161**, 929 (1948).

23) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).
24) C. W. Bunn and E. V. Garner, *Proc. Roy. Soc.*, **A181**, 45 (1947).
25) A. Elliott, E. J. Ambrose and R. B. Temple, *Nature*, **163**, 567 (1949); E. J. Ambrose, A. Elliott and R. B. Temple, *Proc. Roy. Soc.*, **A199**, 183 (1949).
26) R. G. J. Miller and H. A. Willis, *Trans. Faraday Soc.*, **49**, 433 (1953).
27) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Polymer Sci.*, **22**, 227 (1956).

the doubly oriented film, the intensity of the band must be strongest when the angle of incidence, $i=0°$, and must be weaker as i increases (see Fig. 1). On the contrary, in the case when the direction of the transition moment is normal to the rolled plane, the intensity of the band should behave in the reverse manner. Utilizing this fact, it is possible to know the appoximate direction of the transition moment from the results of the absorption measurements on the doubly oriented sample.

The spectra taken with the doubly oriented specimen at different inclinations to the incident polarized beam is partly reproduced in Fig. 2. The relation between the optical density of the bands and the angle of incidence i is also given in Fig. 3.

From these measurements, it was possible to draw the following experimental conclusions: (1) the directions of the transition moments of the CH_2 symmetric stretching band at 2910 cm^{-1} and of the band at 1141 cm^{-1} are preferentially parallel to the surface of the rolled film, and (2) that of the CH_2 antisymmetric stretching band at 2945 cm^{-1} and of the band at 1093 cm^{-1} are more or less normal to the film surface, while (3) those of the other bands do not show any remarkable polarization**** (see Fig. 3).

Prior to the discussion on the nature of 1141 cm^{-1} band, it should be liked to make

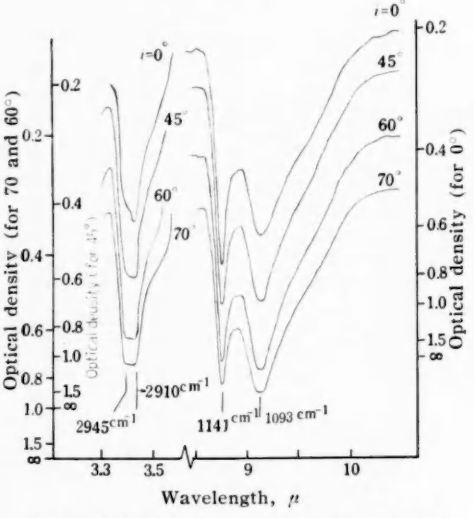

Fig. 2. Infrared spectra of doubly oriented PVA film taken at different inclinations (i means the angle of incidence).

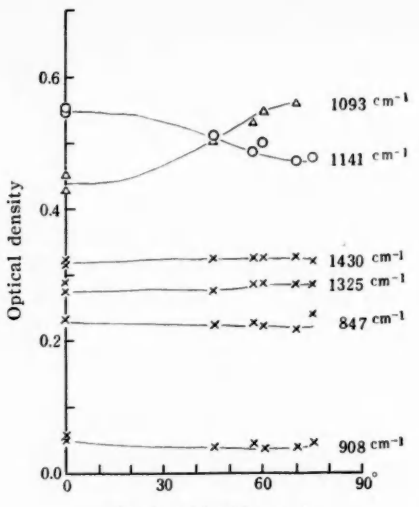

Fig. 3. Relation between the optical density of the bands and the angle of incidence i (doubly oriented PVA film).

CH_2 symmetric stretching 2910 cm^{-1} — CH_2 antisymmetric stretching 2945 cm^{-1}

Fig. 4. Two vibration types of CH_2 stretching of PVA.

a short comment on the modes of vibrations of CH_2 group. As shown in Fig. 4, there are two kinds of C-H stretching vibrations of the CH_2 group of PVA[25]. The transition moment of the symmetric stretching mode at 2910 cm^{-1} should be parallel to the bisector of the angle H-C-H, and that of the antisymmetric mode at 2945 cm^{-1} perpendicular to it. The results on the CH_2 stretching modes inform us of the fact that the plane of the zigzag chain of carbon atoms is parallel to the surface of the film, in agreement with the observation of Ambrose and his coworkers[25].

Krimm, Liang and Sutherland[27] assigned this 1141 cm^{-1} band to the stretching of

**** Of the other bands, 913, 849 and 835 cm^{-1} bands were found to have weak pleochroism by the infrared microspectroscopic measurements on a highly and doubly oriented PVA sample[28].

28) H. Tadokoro, S. Seki, I. Nitta and R. Yamadera, *J. Polymer Sci.*, **28**, 244 (1958).

ether linkage produced by heat-treatment and they stated that the authors' conclusion[20] that this 1141 cm^{-1} band is the crystallization-sensitive band, is open to question. However, the experimental fact presented here together with the following sections b), c) and d) are believed to support the authors' conclusion.

b) Density Consideration. — Of the four samples (Table I) studied in the previous paper[20], sample IV subjected to heat-treatment in air at highest temperature (at 193°C for 2.5 min.) showed a deviation from the linear relationship between the optical density of the 1141 cm^{-1} band and the density of the samples, and this was interpreted as the result of a chemical change on the basis of the ultraviolet absorption spectrum. This deviation was pointed out by Krimm et al.[27] as one of the evidences for their objection to the authors' view[20]. Here, the author wishes to refer to the results of the authors' density measurements by the density gradient tube method on PVA films[29]. The samples for the measurements were treated in silicone oil for various durations at various temperatures as shown in the explanation of Fig. 5. The density of the samples was determined at 25°C by using the mixture of xylene and carbon tetrachloride as flotation medium. The ultraviolet absorption spectra of these samples were also measured with a Beckman Model DU Quartz Spectrophotometer in order to examine whether or not some chemical change occurs. Fig. 5 shows the correlation between the optical density of the 1141 cm^{-1} band and the density of the samples. As the thicknesses of the films were not the same in each case, the relative intensity of the 1141 cm^{-1} band of the samples was obtained by adjusting the intensities of the other bands to fit one another as closely as possible. This procedure was based upon the fact that the intensity of the 1141 cm^{-1} band is very sensitive to heat-treatment, whereas those of others are not. In Fig. 5 the samples denoted by △ show two strong absorption bands (280 and 330 mμ) in the ultraviolet region similarly to that for sample IV in the previous paper[20]. Twelve samples denoted by ○ clearly satisfy the linear relationship, while the samples denoted by △ deviate downwards from this. This fact indicates that this deviation is to be attributed to the thermal decomposition, and so it is less significant in the discussion of the crystallinity of PVA. Thus the observed linear relationship between the intensity of the 1141 cm^{-1} band and the density of the samples is in good agreement with the previous conclusion that the 1141 cm^{-1} band is a crystallization-sensitive band.

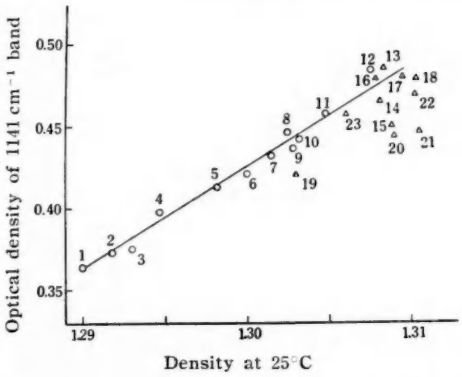

Fig. 5. Optical density of 1141 cm^{-1} band plotted against density for PVA samples subjected to heat-treatments at various conditions in silicone oil[29].

1.	no treatment		13.	180°C	60 min.
2.	100°C	5 min.	14.	190	2
3.	100	100	15.	190	5
4.	140	2	16.	190	21
5.	140	10	17.	220	1
6.	160	5	18.	220	2
7.	160	10	19.	220	15
8.	160	20	20.	240	10 sec.
9.	160	40	21.	240	40
10.	160	85	22.	240	90
11.	180	5	23.	240	120
12.	180	30			

c) Formalization and Swelling in Water. — Fig. 6 shows infrared spectra of dry and swollen PVA samples I and III, and their partial formals. The curves below the swollen samples are for those of the drying process, and were measured successively about 7 min. after the measurement on the swollen sample was done, and so on. In the case of sample I, the 1141 cm^{-1} band was observed to disappear on formalization. On the other hand, for sample III the 1141 cm^{-1} band is not affected remarkably. The 1141 cm^{-1} band of the partial formal of sample III is identified with that of sample III by its similar behavior to deuteration, namely, this band shifts slightly to a shorter wavelength side on deuteration in both cases of PVA and the partial formal of

29) H. Tadokoro, K. Kózai, S. Seki and I. Nitta, ibid., **26**, 379 (1957).

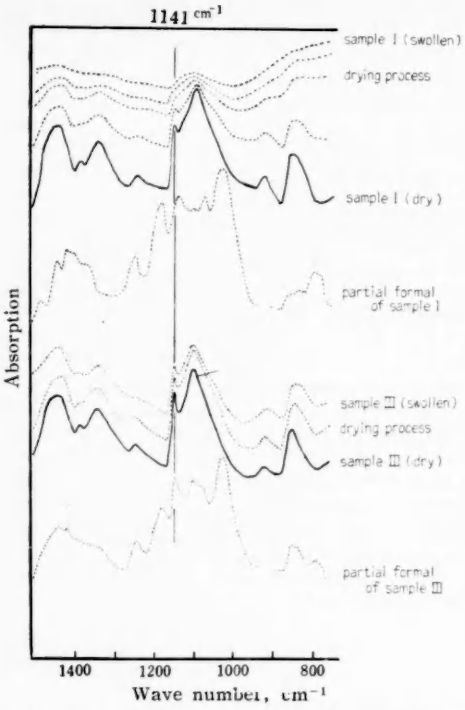

Fig. 6. Infrared spectra of dry and swollen PVA samples I and III and of their partial formals. The curves below the swollen one were measured successively ca. 7 min. after the measurement of the swollen sample was done, and so on.

sample III[30]. The 1141 cm^{-1} band is hardly found in the spectra of the swollen sample I, but appears progressively as the samples are being dried. On the other hand, in the case of sample III this band seems not to be influenced strongly by swelling.

Fig. 7 shows the X-ray photographs of the samples in Fig. 6. In Fig. 7, a) is for dried sample I, b) swollen sample I, c) partial formal of sample I, d) dried sample III, e) swollen sample III, and f) partial formal of sample III. The spots in the photographs a), b) and e) arise from the aluminum foil used for sealing the samples in order to prevent vaporization of water from the samples. The spots in c) and f) are due to the residual sodium sulfate being used for formalization. The haloes in b) and e) are due to liquid water. The diffraction rings due to PVA disappear in photograph b) of the swollen sample I, but the rings seem not to be affected remarkably in the case e) of sample III. In photograph c) of the partial formal of sample I, the intense diffraction rings of PVA give place to a new halo of smaller diffraction angle. This change corresponds to the increase of the apparent lattice distance from 4.51 to 4.72 Å.

The authors' previous observations by use of the infrared absorption and X-ray photographs indicate evidently that the 1141 cm^{-1} band behaves in parallel with the diffraction rings due to the crystalline region of PVA on formalization and swelling in water; namely, both the band and the rings disappear in the case of sample I, but are not affected remarkably in the case of sample III. This fact may also be considered to support the conclusion that this band is a crystallization-sensitive band.

d) On the Assignment of the 1141 cm^{-1} Band.—As to the assigment of the 1141 cm^{-1} band, various interpretations have already been proposed. Elliott and his coworkers[18] explained that this band is connected with the presence of the oxygen atom because of the lack of this band in the case of polyvinyl chloride. Nishino and his coworkers[31] as well as Nagai and his coworkers[32] considered this band to be associated with the formation of hydrogen bond. Krimm and his coworkers[27] suggested that this band may be the stretching of C–O–C linkage produced as the result of the heat-treatment of the sample.

It is considered to be necessary that the assignment of this band should satisfy the following experimental facts:

(1) The strongly perpendicular dichroism of this band (Fig. 4 of Ref. 21).

(2) The fact that the transition moment of the band is nearly parallel to the plane of the zigzag chain (Fig. 2).

(3) The parallel relationship between the intensity of the band and the density of the sample (Fig. 5).

(4) The location of the band in the observed spectrum.

(5) The only slight shift of this band on deuteration (about 7 cm^{-1} or 0.994 in wave number ratio, to higher frequency).

(6) The crystal structure of this substance[22], etc.

As the shift of this band on deuteration is so small, this band seems to be not

30) See Fig. 2 of Ref. 21.

31) Y. Nishino, J. Ukita and T. Kominami, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 159 (1955).

32) E. Nagai and S. Kuribayashi, *Chem. High Polymers* (*Kobunshi Kagaku*), **12**, 322, 368 (1955).

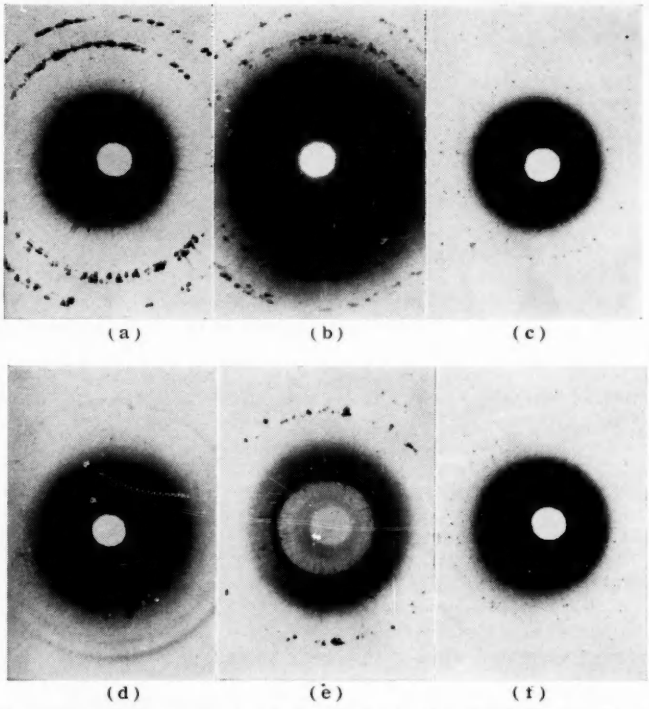

Fig. 7. X-ray photographs corresponding to the samples in Fig. 6: (a) sample I (dry); (b) sample I (swollen); (c) partial formal of sample I; (d) sample III (dry); (e) sample III (swollen); (f) partial formal of sample III.

directly associated with the motion of the hydrogen atom of hydroxyl group such as O–H deformation. The assignment of this band to the stretching of C–O–C linkage does not seem to be able to explain the experimental facts mentioned above [sections a), b) and c)] and the fact that this band exists distinctly even in the spectrum of the sample with no heat-treatment (such a sample is hardly considered to contain ether linkage). In this respect, Haas[33] has recently concluded that (1) the suggestion by Krimm et al.[27] relating this band to C–O–C vibration must be rejected, and (2) a hypothesis which relates the band with some vibrational modes associated only with crystallization is favored.

At the present stage it is still difficult to make the final assignment of this band from the present experimental data, but this band is undoubtedly due to the crystalline arrangements of the molecules and is thought to be intimately related to the regular repetition of the *trans*-configuration of the zigzag chains. For further elucidation of the nature of this band the total syntheses of $-(-CD_2-\underset{\underset{OH}{|}}{CD}-)_p-$ (D) are now being carried out.

The author wishes to express his gratitude to Professor I. Nitta and Assistant Professor S. Seki, under whose guidance this research was carried out. He also expresses his sincere thanks to Professor T. Shimanouchi of the University of Tokyo for helpful advice and criticism, to Dr. T. Kanzawa and Mr. H. Kamio of Takeda Pharmaceutical Industries, Ltd. for preparing part of the charts of the infrared absorption spectra, and to Kurashiki Rayon Co., Ltd. for kindly giving him the PVA samples.

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33) H. C. Haas, *J. Polymer Sci.*, **26**, 391 (1957).

Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. I. Biphenyl

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A twist of a "single" bond in a conjugated system caused by steric effects affects the electronic absorption spectrum of the molecule. Since the interaction of the π-orbitals across the bond and hence the conjugation of the system are maximal when the system is planar, as is well known, any deviation from the planarity of the molecular configuration reduces the degree of conjugation to the corresponding extent, and consequently alters the spectral feature.

The relation between the spatial configuration and the electronic absorption spectrum of a conjugated system may conveniently be divided into the following three kinds; (A) that between the spatial configuration and the shape of the absorption curve (mainly an appearance of fine structure), (B) that between the spatial configuration and the intensity of the conjugation band, and (C) that between the spatial configuration and the position of the conjugation band.

Concerning the relation of A, Merkel and Wiegand[1] proposed the hypothesis that the appearance of fine structure depended on the planarity of the molecular configuration. Thus, the spectra of fluorene and of carbazole, for example, which are thought to be planar, and also that of biphenyl in the crystalline state exhibit fine structures. On the basis of this hypothesis, Merkel and Wiegand suggested that the lack of structure in the spectrum of biphenyl in solution might indicate the non-planarity of the molecule in solution. However, this hypothesis has been denied by Kortüm and Dreesen[2]. According to their opinion, the appearance of fine structure does not depend on planarity of the molecular configuration, but depends rather on its rigidity. However, whether there is an unconditional relation between the molecular configuration and the appearance of fine structure or not has not yet been clarified, since this problem is considerably complicated, and since an appearance of fine structure depends on techniques of measurement, on solvents, etc.

A change in spatial configuration about a "single" bond in a conjugated system has conventionally been thought to affect the position and the intensity of the conjugation band in any of the following three ways, depending on the degree of deviation from the coplanarity[3]: (1) No change in the position of the absorption maximum but a decrease in the intensity. This effect is caused by relatively small twists. (2) A shift of the absorption maximum to shorter wavelengths in addition to a decrease in the intensity. This effect is caused by larger twists than the first effect. (3) When the twist is large enough to eliminate almost completely the $\pi-\pi$ interaction across the twisted bond, the spectrum is similar to the sum of the spectra of the component parts of the molecule on either side of the bond.

On the basis of such a classification, Braude and his coworker[4] assumed the following relation between the angle of twist θ and the molar extinction coefficient ε of the absorption maximum of the conjugation band for the cases of type 1, namely the cases in which the steric effect changes the absorption intensity alone;

$$\varepsilon/\varepsilon_0 = \cos^2\theta$$

where ε_0 is the molar extinction coefficient of the corresponding absorption maximum of the planar reference compound. Braude and his coworkers applied this postulated relation to some sterically hindered derivatives of benzaldehyde[4], of acetophenone[4], of styrene[5], and of biphenyl[6],

1) (a) Chr. Wiegand and E. Merkel, *Ann.*, **557**, 242 (1947). (b) E. Merkel and Chr. Wiegand, *Naturwiss.*, **34**, 122 (1947). (c) E. Merkel and Chr. Wiegand, *Z. Naturforsch.*, **3b**, 93 (1948).

2) G. Kortüm and G. Dreesen, *Chem. Ber.*, **84**, 182 (1951).

3) See, for example: M. S. Newman, "Steric Effects in Organic Chemistry", John Wiley & Sons, Inc., New York (1956), p. 484.

4) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

5) E. A. Braude and F. Sondheimer, ibid., **1955**, 3773.

6) E. A. Braude and W. F. Forbes, ibid., **1955**, 3776.

and stated that the satisfactory value of the angle of twist θ was obtained for each of the compounds. However, it can not be recognized that only a change of the intensity of the conjugation band occurs without any significant displacement of the position in each of the systems of compounds cited by Braude and others, in spite of their assumption. And further, it seems that the derivation of their equation and its basic theory are open to considerable criticism.

However, independently from Braude and others' works, a relation bearing a close similarity to the one mentioned above has been proposed. Thus, Klevens and Platt[7] have stated that the oscillator strength of the conjugation band is linearly related to the van der Waals radius of the interfering group and to the $\cos^2$ of the calculated angle of the C–N bond twist in some ortho-substituted dimethylanilines. In addition, Beale and Roe[8] have found that the changes in oscillator strength of the conjugation band for substitution with methyl groups in stilbene are additive, and that the ortho-substitution reduces the oscillator strength.

Regarding the relation of C, that is, the relation between the spatial configuration of a molecule and the position of the conjugation band, the following examples may be cited: *trans*-Stilbene has the conjugation band at about 294 mμ, which is progressively shifted toward shorter wavelengths with the concurrent decreases in the intensity as one, and then two methyl groups are introduced into the α- and α'-positions of the molecule[9,10]. Biphenyl has the conjugation band at about 247 mμ, which is markedly shifted toward shorter wavelengths in the spectrum of o,o'-dimethylbiphenyl[11]. Further, bimesityl does not exhibit the characteristic conjugation band, but absorbs as two molecules of mesitylene[11,12]. These hypsochromic wavelength displacements are explained in terms of the steric interference of the substituents which prevents the molecule from assuming a coplanar configuration.

Although these phenomena had been known for a considerably long time as the references cited show, no theoretical explanation had been established satisfactorily, and consequently, the quantitative relation between the dimensions of the spatial configuration of the molecule, especially the angle of twist, and the position of the conjugation band had not been clarified[13]. Thus, the prevailing explanations were rather unsatisfactory or unreasonable ones such as, for example, the following: The appearance of the conjugation band is related to the conjugation, and therefore requires the coplanarity of the molecular configuration. On the basis of such an assumption, the hypsochromic shifts observed in, for example, the spectra of α- and α,α'-substituted stilbenes as well as in that of *cis*-stilbene as compared with that of *trans*-stilbene needed to be explained by a rather implausible hypothesis based on a concept of "partial chromophore"[14]. The alternative prevailing explanation was as follows: The extent of the contribution of the dipolar structure in the electronic excited state is larger than in the ground state. Since the dipolar structure requires a coplanarity of the molecular configuration, steric hindrance to such a configuration will raise the potential energy of the excited state more than that of the ground state, and hence, the transition energy will be increased[15].

Previously, the present author calculated the quantitative relations between the degree of deviation from coplanarity of the molecular configuration and the position of the conjugation band as well as the extent of conjugation for stilbenes[16] and also for biphenyls[17,18], by the method based on the simple LCAO molecular orbital method. By the results of the calculations he clarified the fact that the perfect coplanarity is not prerequisite to the occurrence of conjugation and to the appearance of the characteristic conjugation band, and that the conjugation band is gradually shifted toward shorter wavelengths as the degree of deviation from the coplanarity increases. Further he showed that the values of the angle of

7) H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, **71**, 1714 (1949).
8) R. N. Beale and E. M. F. Roe, ibid., **74**, 2302 (1952).
9) (a) H. Ley and F. Rinke, *Ber.*, **56**, 771 (1923). (b) B. Arends, ibid., **64**, 1936 (1931).
10) R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).
11) M. T. O'Shaughnessy and W. H. Rodebush, ibid., **62**, 2906 (1940).
12) L. W. Pickett, G. F. Walter and H. France, ibid., **58**, 2296 (1936).
13) See, for example: (a) R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, **1953**, 2755. (b) W. Klyne, "Progress in Stereochemistry", Vol. 1, Butterworths Scientific Publications, London (1954), p. 142.
14) See, for example: E. A. Braude, *J. Chem. Soc.*, **1949**, 1902. See also Ref. 10.
15) For examples: W. R. Remington, *J. Am. Chem. Soc.*, **67**, 1838 (1945). And also: Refs. 6, and 13b, p. 131.
16) H. Suzuki. This Bulletin, **25**, 145 (1952).
17) H. Suzuki, ibid., **27**, 597 (1954).
18) H. Suzuki, ibid., **29**, 945 (1956).

twist as well as the effective resonance energy can be satisfactorily computed from the observed position of the conjugation band.

Although these previous treatments seem fairly satisfactory in principle, it was found afterwards that they included an inadequate assumption. Thus, the choice of the absorption maximum corresponding to the planar molecule of biphenyl in the previous paper[17] was found to be probably inadequate. In addition, it seems that there are some aspects which were not given adequate consideration in the previous papers. Thus, first, the spectrum of *trans*-stilbene in solution was assumed to be that of the planar molecule of the compound without sufficient consideration. Strictly speaking, there is no evidence to indicate that *trans*-stilbene in the solution state has the planar configuration. Secondly, the electronic bathochromic effects of substituents such as methyl groups were ignored, and this ignoring seems to be an over-simplification. These electronic effects of substituents should not be ignored particularly when the substituents are on the benzene nuclei. Lastly, the position of absorption maximum varies more or less with the solvent, so the solvent effect should also be taken into account.

In this series of papers, the erroneous assumption mentioned above being corrected, and the aspects which were not given sufficient consideration being re-examined, a method similar to the previous one is applied to the greater range of conjugated compounds, and the relation between the spatial configuration of the molecule and the electronic absorption spectrum, especially the position of the conjugation band, is discussed more comprehensively and more fully. The relation of the intensity of the band and that of the appearance of fine structure to the spatial configuration of the molecule will also be referred to at suitable places in this series.

The present series is concerned mainly with the spatial configurations and the electronic states of the molecules in solution. This subject is certain to be very important in studying the relations between molecular structures and reactivities of organic compounds. In this connection, it seems that there is no precise and direct means to determine the spatial configurations of molecules in solution, such as the X-ray analysis for the crystalline states or the electron diffraction analysis for the vapor states. Therefore, information from the analysis of the electonic absorption spectra is conceivably important and useful in this respect. From this point of view, in this series the spatial configurations of the compounds inferred from the electronic absorption spectra are correlated as much as possible with the other properties, especially the reactivities of the compounds.

In this part of series, the ultraviolet absorption spectra of biphenyl in the various states, i.e. the crystalline, the solution, and the vapor state, and their relations to the spatial configurations of the molecule are discussed in detail as the basis of the present treatment.

Calculation

Although the procedures of calculation were already outlined in the previous papers[16,17], those for biphenyl are shown below in somewhat more refined form.

(1) Correlation of a Parameter for the Resonance Integral for the Pivot Bond with the Bond Length and the Interplanar Angle. — The π—π resonance integral for the 1-1′ bond, namely the co-annular or pivot bond, is denoted by $\mu\beta$, in which β is the π—π resonance integral for the C-C bond in the benzene ring and μ is a parameter by which allowance is made for changes of the resonance integral with the bond length and the angle of twist, i.e. the angle between the planes of the two benzene rings, which is subsequently referred to also as the interplanar angle. (The symbol α in the previous papers was replaced by μ.)

The π—π resonance integral for C-C bond can be taken to be approximately proportional to the π—π overlap integral[19], and, as easily verified, the π—π overlap integral $S(R, \theta)$ in the case where the bond length is R and the angle of twist is θ is equal to the overlap integral $S(R, 0°)$ in the case where the bond length is R and the angle of twist is 0°, multiplied by $\cos\theta$. Accordingly, the parameter μ can approximately be expressed by the following equation;

$$\mu = S(R, 0°)\cos\theta / S(1.39, 0°) \qquad (1)$$

where $S(1.39, 0°)$ represents the π—π overlap integral for the C-C bond in the benzene ring, the length of which is 1.39 Å.

The relation between the bond length R and the corresponding overlap integral $S(R, 0°)$ can be obtained from Mulliken's Tables[20]. According to results of calculation based on the tables, the values of $S(R, 0°)$ and hence of $S(R, 0°)/S(1.39, 0°)$ vary linearly with R, at least in the range of R

19) (a) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941). (b) J. van Dranen and J. A. A. Ketelaar, *J. Chem. Phys.*, **17**, 1338 (1949).

20) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, ibid., **17**, 1248 (1949).

between 1.44 and 1.54 Å, and the relations can approximately be expressed as follows:

$$S(R,0^\circ)=0.1920+(1.54-R)\times 0.36 \quad (2)$$

$$S(R,0^\circ)/S(1.39,0^\circ)=0.77108+(1.54-R)\times 1.4458 \quad (3)$$

where the value of $S(1.39,0^\circ)$ is 0.249.

According to the result of X-ray crystal analysis by Dhar[21], R is 1.48 Å and θ is 0° in biphenyl in the crystalline state. Consequently, the corresponding value of μ is evaluated at 0.858.

Any deviation from the coplanar configuration must inevitably reduce the π—π interaction across the co-annular bond to the corresponding extent, and consequently must be accompanied by change in the bond length. Thus, the value of R will vary from 1.48 Å in the planar biphenyl molecule to 1.54 Å, i. e. the length of the normal C-C single bond, as θ varies from 0° to 90°. Therefore, the following relation may tentatively be assumed between R and θ:

$$\{S(R,0^\circ)-S(1.54,0^\circ)\}/\{S(1.48,0^\circ)-S(1.54,0^\circ)\} = S(R,\theta)/S(R,0^\circ)=\cos\theta \quad (4)$$

Hence, evidently from Eq. 2,

$$R=1.54-(1.54-1.48)\times\cos\theta \quad (5)$$

Then, from Eqs. 1 and 4 one obtains;

$$\mu=\cos\theta\times S(1.54,0^\circ)/S(1.39,0^\circ) +\cos^2\theta\times\{S(1.48,0^\circ)/S(1.39,0^\circ) -S(1.54,0^\circ)/S(1.39,0^\circ)\} \quad (6)$$

And further, from Eqs. 3 and 6

$$\mu=\cos\theta\times 0.77108+\cos^2\theta\times(1.54-1.48)\times 1.4458 \quad (7)$$

It is evident that the value of μ becomes gradually smaller as the value of θ becomes larger and that μ becomes 0 when θ is 90°.

(2) Solution of the Secular Equation for the Determination of the Molecular Orbitals. — By solving the secular equation for the determination of the molecular orbitals as linear combinations of $2p\pi$ atomic orbitals, one can obtain the values of energies of the molecular orbital corresponding to the value of the parameter μ. Consequently, the values of the extra-resonance energy (subsequently referred to as *R.E.*), of the coefficients of the $2p\pi$ atomic orbitals in the molecular orbital functions, and of the quantities such as the π-bond orders corresponding to the molecular configuration prescribed by the value of μ can also be obtained by the usual procedures[22].

The biphenyl molecule can be considered as belonging to the symmetry group D_2. Then, the highest occupied π-orbital (π_1) in the biphenyl molecule belongs to the representation B_3, and coincides with the φ_1 orbital in benzene when μ is 0. On the other hand, the lowest vacant π-orbital (π_1^*) belongs to A_1, and coincides with the φ_2 orbital in benzene when μ is 0. (The notation for orbitals in benzene is according to Sklar[23].) Transitions from orbitals belonging to B_2 to those belonging to A_1 are allowed by absorption of light polarized along the direction of the long-axis of the molecule. Accordingly, the energy difference (referred to as ΔE_A) between the lowest vacant orbital π_1^* and the highest occupied orbital π_1 is considered to be the transition energy corresponding to the conjugation band (the A-band) in the spectrum of biphenyl.

In addition to the eight orbitals belonging to B_1 and B_3, energies of which vary with μ, there are two sets of doubly degenerate orbitals belonging to A_1 and B_2, energies of which do not vary with μ. These orbitals may be considered as ones localized in the benzene rings. Thus, the two of these orbitals whose energy is $+\beta$ (φ) correspond to the φ_{-1} orbital in benzene, and another two whose energy is $-\beta$ (φ^*) correspond to the φ_{-2} orbital in benzene. In other words, it can be considered that one orbital of each of the two sets of doubly degenerate orbitals in each benzene ring interacts with the neighboring π-orbitals to give whole-molecular orbitals when two benzene rings are linked with each other, whereas the other orbital of each set remains isolated. The intense bands observed at about 200 mμ in the spectra of biphenyl and its related compounds are presumably due to transitions between the orbitals localized in the benzene rings.

The results of calculations are shown in Table I. In this table, $\Delta E_A(-\beta)$ and $R.E.(-\beta)$ are values obtained by ignoring the π—π overlap integral, and $\Delta E_A(-\gamma)$ and $R.E.(-\gamma)$ are values obtained by taking the overlap integral into account, assuming the value of the overlap integral for the C-C bond in benzene as 0.25. The symbol $p_{1-1'}$ represents the π-bond order of the 1-1' bond.

It is evident that the values of ΔE_A increase as the value of μ decreases, and agree with the values for benzene when μ is 0. This means that the conjugation band is gradually shifted toward shorter wavelengths as the value of μ decreases, and therefore as the value of θ increases, and that the band will coincide with that of benzene when μ is 0 and therefore θ is 90°.

It appears that there is no simple quantitative relation between μ and ΔE_A, or between ΔE_A and *R.E.* On the other hand, examination of the data in Table I reveals that *R.E.* $(-\beta)$ is almost completely proportional to μ^2 and can approximately be expressed as $0.385\times\mu^2$, a fact which coincides with the qualitative generalization by Dewar[24]. In addition, $p_{1-1'}$ is roughly proportional to μ and can roughly be expressed as

21) (a) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932); *Chem. Abstr.*, **26**, 4517 (1932). (b) J. Dhar, *Proc. Natl. Inst. Sci. India*, **15**, 11 (1949); *Chem. Abstr.*, **43**, 4655 (1949).

22) See, for example: H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1944), p. 254 ff. See also: C. A. Coulson, "Valence", Clarendon Press, Oxford (1952), p. 250 ff.

23) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

24) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952). (*Theorem 14*).

TABLE I

μ	1.1	1.0	0.9	0.8	0.7	0.6
$\Delta E_A(-\beta)$	1.3610	1.4092	1.4596	1.5120	1.5666	1.6232
$\Delta E_A(-\gamma)$	1.4016	1.4544	1.5099	1.5680	1.6290	1.6929
$R.E.(-\beta)$	0.4606	0.3832	0.3128	0.2484	0.1914	0.1414
$R.E.(-\gamma)$	0.1416	0.1184	0.0972	0.0774	0.0600	0.0446
$p_{1-1'}$		0.370	0.334	0.298	0.264	0.228
μ	0.5	0.4	0.3	0.2	0.1	0
$\Delta E_A(-\beta)$	1.6820	1.7424	1.8048	1.8686	1.9338	2
$\Delta E_A(-\gamma)$	1.7598	1.8292	1.9016	1.9764	2.0538	2.1333
$R.E.(-\beta)$	0.0988	0.0632	0.0358	0.0160	0.0040	0
$R.E.(-\gamma)$	0.0312	0.0200	0.0114	0.0052	0.0014	0
$p_{1-1'}$	0.193	0.156	0.118	0.079	0.040	0

$0.375\times\mu$. The value of $p_{1-1'}$ is 0.319 when μ is 0.858.

(3) Correlation of the Calculated Transition Energy with the Observed Position of the Conjugation Band. — The present calculations are concerned with the vertical excitations according to the Franck-Condon principle, namely, to electron jumps without change in the configuration of the molecular skeleton.

In general, the most probable spatial configuration of a conjugated compound and its stability are believed to be determined mainly by the combined effect of the resonance stabilization and the steric repulsion. The steric repulsion will raise the potential energy of the molecule in the ground state. Accordingly, in the problem which is concerned with, for example, the difference of stability between the geometrical isomers, the steric repulsion energy must be taken into account in principle.

On the other hand, since the spatial configuration of the molecule is assumed not to change between in the ground state and in the electronic excited state, the magnitudes of the steric repulsion energies involved in both the states may be the same at least approximately, and therefore, it seems that the electronic transition energy must not contain any significant contribution of the steric repulsion energy itself, and must be determined as a function of the spatial configuration of the molecule alone. That is, the values of ΔE_A shown in Table I may be correlated directly with the observed wave numbers of the absorption maxima of the conjugation bands. (In this connection, the interpretations by Braude and others on the relation between the steric effect and the position of the conjugation band are highly questionable. This will be referred to in detail in later parts of this series.)

The correlation of the calculated transition energy ΔE_A with the observed position ν_A (in wave number) of the conjugation band is accomplished as follows. When there are two compounds whose spatial configurations are already known and whose corresponding electronic absorption spectra are already observed, the linear relation of ΔE_A to ν_A is assumed between the two points prescribed by the two reference compounds.

As one of the two reference compounds, the planar compound is chosen in most cases. This is subsequently referred to as the longer-wavelength-side reference compound. The corresponding ΔE_A and ν_A are denoted by ΔE_L and ν_L, respectively. On the other hand, as the shorter-wavelength-side reference compound the one which corresponds to the value 0 of the parameter μ or the analogous one is chosen in most cases. The corresponding ΔE_A and ν_A are denoted by ΔE_S and ν_S, respectively. Then, the value of ΔE_A for a given compound of the type under consideration is obtained from the observed value of ν_A by the following equation:

$$\Delta E_A = \Delta E_S - (\Delta E_S - \Delta E_L)(\nu_S - \nu_A)/(\nu_S - \nu_L) \quad (8)$$

Consequently, the corresponding value of μ and then the values of θ, R, $R.E.$, etc. can be calculated in turn.

In the case of biphenyl, biphenyl in the crystalline state is chosen as the longer-wavelength-side reference compound. In this molecule, θ is 0°, and R is 1.48 Å as mentioned already, and consequently, the corresponding values of μ and of ΔE_A (i.e. ΔE_L) are computed to be 0.858 and $1.482(-\beta)$, respectively. On the other hand, as the shorter-wavelength-side reference compound, benzene is chosen, which corresponds to the case where the values of μ and of ΔE_A (i.e. ΔE_S) are 0 and $2(-\beta)$, respectively. However, it requires sufficient consideration to determine what values of ν are to be taken as ν_L and ν_S, corresponding to ΔE_L and ΔE_S, respectively. Therefore, these choices of the references are discussed in detail in the next sections.

The Shorter-wavelength-side Reference

When the value of the parameter μ is 0, the energy levels in biphenyl coincide with those in benzene, and the value of ΔE_A (i.e. ΔE_S) is $2(-\beta)$. According to Platt[25], the "center of gravity of singlets", 48000 cm^{-1} in the absorption spectrum of benzene, that is, the weighted mean of the energies of the three singlet-singlet transitions at 48000 cm^{-1} (208.3 mμ, B_{1u}), at 38200 cm^{-1} (261.8 mμ, B_{2u}), and at 53000 cm^{-1} (188.7 mμ, E_{1u}) measured in solution[26], corresponds to the energy

25) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).
26) H. B. Klevens and J. R. Platt, ibid., **17**, 470 (1949).

difference of $2(-\beta)$ calculated by the molecular orbital method of the same order of approximation as the present treatment. Therefore, the value of 48000 cm^{-1} was taken as ν_S in the previous papers.

The same assumption is used also in the present treatment, since this assumption seems to be supported by the following facts. First, Dewar[27] has used the value of 208 mμ for the wavelength of the band of benzene in his application of the NBMO method to spectra of catacondensed aromatic compounds. Secondly, Dale[28] has used a value of about 205 mμ for benzene in his attempt to correlate the wavelength positions of the main bands of linear polyphenyls with the numbers of linked chain benzene nuclei. Furthermore, according to Wenzel[29], the intense conjugation band at about 250 mμ in the spectrum of biphenyl corresponds to the band at about 210 mμ of benzene. All these values for benzene are closely similar to the "center of gravity of singlets" mentioned above.

The Longer-wavelength-side Reference

Spectra of Biphenyl in the Crystalline State.— The value of ΔE_A (i. e. ΔE_L), $1.482(-\beta)$, calculated by using the values of the dimensions of the spatial configuration of biphenyl in the crystalline state is to correspond to the wave number of the absorption maximum of the conjugation band of the "isolated" planar molecule of biphenyl. The spectrum of biphenyl in solution has the conjugation band at about 247 mμ, but this band should not be taken as the band corresponding to ΔE_L, because there is no evidence to indicate that the molecule of biphenyl in solution would have the same spatial configuration as in the crystalline state. In the earlier paper[17], the wave number 36306 cm^{-1} of the first absorption maximum in the spectrum of biphenyl in the crystalline state measured by Deb[30] was taken as ν_L, i. e. the wave number corresponding to ΔE_L. According to Deb, the characteristic (conjugation) band in the spectrum of biphenyl in the liquid state is split up into two broad bands at 36306 cm^{-1} (2754 Å) and at 37386 cm^{-1} (2675 Å) in the spectrum of the solid at 30°C, and the band at 36306 cm^{-1} was presumed to be the intrinsic band. This assignment of the band is evidently inadequate, in view of the studies by Wenzel[29] and by Dale[28].

Wenzel[29] has proposed the hypothesis that the intense transition at about 250 mμ in biphenyl in solution is interpreted as a superposition of a strong and a weak transition corresponding to the 210 mμ and the 260 mμ transition in benzene, respectively. According to her, the weak transition is hidden by the strong one in the spectrum of biphenyl in solution. From comparison of spectra of some 3- and 3,3'-substituted biphenyl derivatives with pairs of spectra of benzene and the correspondingly substituted benzene derivatives and with pairs of spectra of naphthalene and its correspondingly substituted derivatives, she has inferred that the "hidden transition" of biphenyl may be located at about 275 mμ or at about 271 mμ, and that the intensity of this transition may be of the same order as the weak transitions in benzene and naphthalene.

The existence of the hidden transition in biphenyl has experimentally been corroborated by Dale[28]. He has measured the spectrum of biphenyl in the crystalline state by the pressed KCl-disk technique, and found that the spectrum is very similar to the solution spectrum. Thus, the spectrum of the solid showed an intense, structureless band with a maximum at 253 mμ, which is to be compared with the band at about 246 mμ in the solution spectrum. On the other hand, the spectra measured on thin films of solidified melt, on those by evaporation of a thin layer of solution, and on those of sublimed crystals of biphenyl revealed a band showing fine structure with a maximum at about 275 mμ. The molar extinction coefficient of the absorption maximum has been very roughly estimated to be about 1000~2000. In addition, whereas the spectra of *p*-terphenyl and of *p,p'*-quaterphenyl either in solution or in the crystalline states measured by the pressed KCl-disk technique showed the intense bands without structure at considerably longer wavelengths than that of biphenyl, the spectra of solidified melts or sublimed crystals of these compounds showed bands with structure at about 275 mμ, similarly to the corresponding one of biphenyl. These weak bands at about 275 mμ are probably due to the transversely polarized transitions normally hidden by the stronger conjugation bands. This revelation of the hidden transitions in biphenyl and *p*-polyphenyls has been interpreted as follows. Since the incident light is almost parallel to the long molecular axes in the thin films of crystals prepared by solidification of melts, by evaporation of solutions, or by sublimation, owing to the orientation of molecules in these samples, the conjugation bands due to transitions polarized along the long molecular axes are so reduced that the weak hidden transitions are revealed.

In view of the evidences mentioned above, the band at about 275 mμ in the spectrum of the solid biphenyl measured by Deb[30] is probably the "hidden transition". In this connection, Merkel and Wiegand[1] reported that the spectrum of biphenyl in the crystalline state exhibited a band showing fine structure in sharp contrast with that in the solution, and assumed this fact as one of the bases for their hypothesis concerning the relation between the appearance of fine structure and the coplanarity of the molecular configuration. Probably they compared impertinently the "hidden transition" revealed in the solid spectrum with the conjugation band in the solution spectrum.

Besides the bands at about 275 mμ and at 267 mμ mentioned above, Deb[30] found a very feeble band at about 290 mμ with structure in spectra

27) M. J. S. Dewar, *J. Chem. Soc.*, **1952**, 3532.
28) J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).
29) A. Wenzel, *J. Chem. Phys.*, **21**, 403 (1953).
30) A. R. Deb, *Indian. J. Phys.*, **27**, 305 (1953).

of biphenyl measured on the liquid films and on the solid films of larger thickness. This feeble band was resolved as sharp absorption peaks when the temperature of the solid film was reduced to −180°C. Deb has assumed that this feeble band at about 290 mμ belongs to a system different from the one to which the bands at 275 mμ and at 267 mμ belong, and that this feeble system is due to the transition in one of the two benzene rings in biphenyl when the second one is in the excited state. Perhaps the same feeble band at about 290 mμ was recently found by Coffman and McClure[31] and by Broude and his collaborators[32] in the spectrum of a single crystal of biphenyl at 20°K with polarized light, and also by Kanda[33] in the spectrum of the solution at low temperature. In addition, biphenyl appears to have a very feeble band at longer wavelengths than 300 mμ. Although the assignments of these feeble bands have not yet been established with certainty, it may be safe to say that these bands are to be excluded from the present consideration.

Although it may be somewhat open to criticism that the state of biphenyl in the pressed KCl-disk is the same as that in the crystal, it is assumed to be so. Then, from the above considerations, the intense band detected by the pressed KCl-disk technique may be taken as the conjugation band of the planar molecule of biphenyl in the crystalline state. Consequently, one would assume that the wave number 39526 cm^{-1} (253 mμ) of the position of the maximum might be ν_L, corresponding to the calculated transition energy $1.482(-\beta)$, ΔE_L, for the planar molecule of biphenyl. However, there is the possibility that interactions between the molecules in the crystal may affect the energy levels in the molecule and consequently the absorption spectrum of the compound. Accordingly, although such intermolecular interactions are supposed to be weak in nonpolar aromatic crystals[34], it is necessary to make allowances for this effect in the choice of the references for the correlation between ν_A and ΔE_A.

Normal Red-shift.—According to the results of measurements by Dale[25], the absorption maximum in the spectrum measured by the pressed KCl-disk technique is always at longer wavelengths than the corresponding one in the spectrum of the solution. The magnitude of the wavelength displacement of a band of a rigid molecule due to the change of the state from the solution in hexane to the solid state, which was referred to as the "normal red-shift", was found to vary regularly with the wavelength of the corresponding band, by measuring the spectra of naphthalene and of anthracene in both the states. Thus, the normal red-shift increases regularly from about 2 mμ at 220 mμ to 8 mμ at 300 mμ, and to 19 mμ at 400 mμ, with increasing wavelength of the position of the band. This normal red-shift is supposed to be due to the effect of interactions between the molecules in the crystals. From the analogy of the solvent effect[35] and of the Davydov effect[36-41] in a single crystal, it would be expected that the magnitude of the normal red-shift might be related to the intensity of the band. But, in fact, it is not so. The band cited by Dale includes the bands of considerably different intensity from each other, and no regularity between the magnitude of the normal red-shift and the intensity of the band can be found. Thus, the logarithms of the molar extinction coefficients of the bands of naphthalene at about 275 mμ and at about 221 mμ are 3.82 and 5.02, respectively[42], and the oscillator strengths of these bands are 0.11 and 1.7, respectively[41]. The logarithms of the molar extinction coefficients of the bands of anthracene at about 376 mμ and at about 252 mμ are 3.88 and 5.25, respectively[42], and the oscillator strengths of these bands are 0.1 and 2.3, respectively[37]. And further, according to Craig and others, the band of naphthalene[41] at about 275 mμ and that of anthracene[37-39] at about 380 mμ are assigned as "short-axis transitions", and that of naphthalene at about 220 mμ and that of anthracene at about 250 mμ are assigned as "long-axis transitions". From these considerations, the regular relation between the magnitude of the normal red-shift and the wavelength of the position of the absorption band seems to hold regardless of kinds of compounds, of characters of bands, and of intensities of bands. Accordingly, by application of this relation, the magnitude of the normal red-shift corresponding to the wavelength 253 mμ of the maximum of the conjugation band in the spectrum of biphenyl in the crystalline state (measured by the pressed KCl-disk technique) may be estimated to be about 3.5 mμ. (The oscillator strength of the conjugation band of biphenyl is 0.411 in solution, according to Almasy and Laemmel[43].)

On the other hand, according to the results of the measurements by the present author, which will be reported in detail in Part V of this series, the intense bands at 294.1 mμ and at 306.9 mμ in the spectrum of *trans*-stilbene in *n*-heptane are shifted toward longer wavelengths by about 4.5 mμ and by about 5.5 mμ, respectively, in the spectrum measured by the pressed KCl-disk

31) R. Coffman and D. S. McClure, *Can. J. Chem.*, **36**, 48 (1958); D. S. McClure, ibid., **36**, 59 (1958).
32) V. L. Broude, E. A. Izrailevich, A. L. Liberman, M. I. Onoprienko, O. S. Pakhomova, A. F. Prikhot'ko and A. I. Shatenshtein, *Optika i Spektroskopiya*, **5**, 113 (1958).
33) Yoshiya Kanda (Kyushu Univ.), a personal communication.
34) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).
35) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).
36) (a) A. S. Davydov, *Zhur. Eksptl. Teoret. Fiz.* (*J. Exptl. Theoret. Phys.*), **18**, 210 (1948). (Translated by M. Kasha.) (b) V. L. Broude, V. S. Medvedev and A. F. Prikhot'ko, ibid., **21**, 665 (1951). (c) A. S. Davydov, ibid., **21**, 673 (1951).
37) D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, **1955**, 539.
38) D. P. Craig, ibid., **1955**, 2302.
39) D. P. Craig and P. C. Hobbins, ibid., **1955**, 2309.
40) D. P. Craig and J. R. Walsh, *J. Chem. Phys.*, **25**, 588 (1956).
41) D. P. Craig and J. R Walsh, *J. Chem. Soc.*, **1958**, 1613.
42) E. Clar, *Spectrochim. Acta*, **4**, 116 (1950).
43) F. Almasy and H. Laemmel, *Helv. Chim. Acta*, **33**, 2092 (1950).

TABLE II. ULTRAVIOLET ABSORPTION SPECTRA OF BIPHENYL IN VARIOUS SOLVENTS

Solvent	A-band		B-band		C-band	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
n-Heptane	247.0	16450	(205.0)	41400	200.5	45100
Methanol	247.2	17300	—		—	
95% Ethanol	247.7	18050	(204.5)	42000	201.5	43000
Chloroform	249.5	16700	—		—	
Carbon tetrachloride	256.5	16450	—		—	

Wavelengths (mμ) in parentheses denote inflections.

technique. (The oscillator strength of the conjugation band in the spectrum of *trans*-stilbene in solution is 0.745, according to Beale and Roe[5].) These values, probably corresponding to the normal red-shifts of the conjugation band of *trans*-stilbene, are considerably smaller than those (about 8 and 9 mμ) anticipated from the relation mentioned above between the shift and the position of the band.

The crystals of naphthalene[41], anthracene[37], biphenyl[44], and *trans*-stilbene[44,45] all belong to the monoclinic space group C_{2h}^5, and bear a certain similarity to each other. However, whereas in each of these compounds except for the last the number of molecules in a unit cell is 2, in the crystal of *trans*-stilbene the number of molecules in a unit cell is 4. On the other hand, the molecular structure of biphenyl may be said to have greater similarity to that of *trans*-stilbene than to those of naphthalene and anthracene. From such considerations, it seems that there may be a possibility that the magnitude of the normal red-shift of the conjugation band of biphenyl is smaller than the value estimated above and is probably about 2 mμ, on the analogy of the case of *trans*-stilbene.

Since the estimation of the magnitude of the normal red-shift of the conjugation band of the "planar" molecule of biphenyl, at any rate, includes inevitable uncertainty, the alternative values of 3.5 and 2 mμ are assumed in the present calculation. After being corrected for the normal red-shift by these values, the position of the absorption maximum of the conjugation band of the "isolated" planar biphenyl molecule is assumed to be 249.5 mμ (a) or alternatively 251 mμ (b), and the corresponding wave numbers, (a) 40080 cm^{-1} and (b) 39841 cm^{-1}, are assumed to be ν_L.

The difference between the above assumed position of the conjugation band of the "isolated" planar biphenyl molecule, 249.5 or 251 mμ, and the corresponding one of biphenyl in solution, 247 mμ (in *n*-heptane, the present work) or 246 mμ (in hexane[25]), is assumed to be due to the difference in the most probable spatial configuration of the molecule between in the solution state and in the crystalline state.

44) J. Hengstenberg and H. Mark, *Z. Kristallogr. Kristallgeometr., Kristallphysik. Kristallchem.*, **70**, 283 (1929); *Chem. Zentr.*, **C1**, 3968 (1930).

45) (a) J. M. Robertson, M. Prasad and I. Woodward, *Proc. Roy. Soc.* (London), **A154**, 187 (1936). (b) J. M. Robertson and I. Woodward, ibid., **A162**, 568 (1937).

Spectra of Biphenyl in Solution

The ultraviolet absorption spectra of biphenyl in various solvents measured by the present author on a Cary recording spectrophotometer Model 14 M-50 are shown in Table II and Fig. 1. In Fig. 1, the spectra of biphenyl in the crystalline state and in the vapor state found in the literature are also shown for comparison.

The band represented as A-band in Table II is the conjugation band (the so-called K-band). The C-band is the one presumably due to transitions between the orbitals localized on each of the benzene rings, as already mentioned. The B-band (inflection) is probably the vestigial band due to transitions from the highest

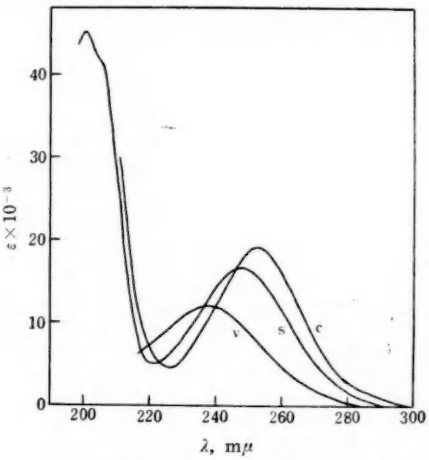

Fig. 1. Ultraviolet absorption spectra of biphenyl in various states.
c. The crystal spectrum measured by Dale[25] by the pressed KCl-disk technique. (The extinction scale is arbitrary for the reliable absolute extinction value could not be obtained.)
s. The solution spectrum (solvent: *n*-heptane).
v. The vapor spectrum measured by Almasy and Laemmel[43] at 170°C.

occupied orbital $\pi_1(B_2)$ to the orbitals φ^* belonging to A_1 or B_2 whose energy is $-\beta$, or from the orbitals φ belonging to A_1 or B_2 whose energy is $+\beta$ to the lowest vacant orbital $\pi_1^*(B_1)$.

It is seen that the spectrum is affected more or less by the solvents. Thus, the conjugation band at 247 mμ in the spectrum of the solution in *n*-heptane is shifted more or less toward longer wavelengths in the spectra in other solvents. The magnitude of the bathochromic shift by the solvent effect is small in methanol and in ethanol, is considerably larger in chloroform, and is extraordinarily large in carbon tetrachloride. In view of these solvent effects, data of spectra in the same solvent should in principle be compared at least in each of the systems of compounds in the treatment. In this part, the data of the spectra in non-polar hydrocarbon solvents being taken as the basis for comparison, and being corrected for the wavelength displacements of the band resulting from changes in phase (i.e. the normal red-shift mentioned above for the crystalline state and the solvent effect for the vapor state which will be mentioned later), the data of the spectra of biphenyl in the various states are compared.

Since the difference of the solvent effect between that of *n*-heptane and of *n*-hexane is supposed to be very small, the difference between the result of the measurement by the present author using *n*-heptane as solvent and that by Dale[28] using *n*-hexane as solvent may be ascribed to experimental errors. At any rate, the position of the maximum of the conjugation band in the spectra of biphenyl in the non-polar hydrocarbon solvents is located at slightly shorter wavelengths than that assumed above for the "isolated" planar molecule of biphenyl. This fact may be supposed to indicate that the most probable conformation of the molecule of biphenyl in solution is slightly non-planar, agreeing with the inference by Dale[16] from comparison of the results of measurements of the infrared absorption spectra of biphenyl in the solutions and in the pressed KBr-disk.

Spectra of Biphenyl in Vapor State

The spectra of biphenyl in the vapor state were studied thoroughly by Almasy and Laemmel[13]. They measured the spectra of biphenyl vapor at the various temperatures from 170 to 520°C and investigated also effects of various foreign gases.

It is noteworthy that the spectrum of pure biphenyl vapor is not largely affected by temperature at least in the range mentioned above, and that whereas the intensity ε of the absorption maximum of the conjugation band decreases gradually from 12050 at 170°C to 9400 at 520°C when the temperature is raised, the oscillator strength of the band is maintained almost constant regardless of the temperature. (The oscillator strength at 170°C is 0.316. The average of the values at 170, 260, 360 and 520°C is 0.311 ± 0.0035.)

The position of the absorption maximum is gradually shifted toward longer wavelengths from 42000 cm^{-1} at 170°C to 41750 cm^{-1} at 520°C, as the temperature is raised. From these results, the position of the maximum at 20°C was inferred by extrapolation as 42100 cm^{-1} (ε, 19000).

Whereas these spectra of the vapor, showing no fine structure, resemble in shape the spectra of the solutions and that of the crystal by the pressed KCl-disk technique, the absorption maximum is considerably shifted toward shorter wavelengths in the vapor spectra than in the solution spectra, and further than the assumed position of the maximum for the "isolated" planar molecule. This fact is supposed to indicate that the degree of deviation from the planarity of the molecular configuration is larger in the vapor state than in the solution state.

Correction for Solvent Effect.—In order to compare the position of the absorption maximum in the vapour spectrum with that in the solution spectrum and with that for the "isolated" planar molecule, the solvent effect must be taken into account.

According to Bayliss[35], the magnitude of the displacement $\Delta\nu$ (in cm^{-1}) of the absorption maximum of a nonpolar molecule to lower frequencies by a nonpolar solvent is related to the refractivity of the solvent, and is expressed as the following equation:

$$\Delta\nu = \frac{3e^2}{8\pi^2c^2m}\cdot\frac{f}{\nu a^3}\cdot\frac{n^2-1}{2n^2+1} = 10.71\times10^9\,\frac{f}{\nu a^3}\cdot\frac{n^2-1}{2n^2+1}$$

where n is the refractive index of the solvent at the frequency concerned, f is

46) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

TABLE III. RESULTS OF CALCULATIONS FOR BIPHENYL IN VARIOUS STATES

State	λ_{max}, mμ	ν_{max}, cm^{-1}	ΔE_A, $-\beta$	μ	$\theta°$	R, Å	$R.E.$, $-\beta$
Crystal	a) 249.5*	40080	1.482	0.858	0	1.48	0.286
	b) 251*	39841	〃	〃	〃	〃	〃
Solution	247.0	40486	a) 1.509	0.807	19	1.484	0.253
	(*n*-heptane)		b) 1.523	0.780	23	1.485	0.237
	246	40650	a) 1.519	0.787	22	1.485	0.241
	(*n*-hexane)		b) 1.533	0.762	26	1.486	0.227
Vapor	238.8**	41866	a) 1.599	0.643	40	1.494	0.163
	(170°C)		b) 1.611	0.621	42	1.495	0.152
	238.3**	41966	a) 1.605	0.631	41	1.495	0.157
	(20°C)		b) 1.617	0.611	43	1.496	0.147

* Values corrected for the normal red-shift.
** Values corrected for the solvent effect.

the oscillator strength of the band, ν is the wave number of the position of the absorption maximum, and a is the radius of the (spherical) solute molecule. This relation was experimentally verified by Coggeshal and Pozefsky[47] in their study on the spectra of naphthacene and some other cata-condensed aromatic hydrocarbons. By application of this equation, the magnitude of the shift toward lower frequencies of the maximum of the conjugation band of biphenyl resulting from change in the state from the vapor to the solution in *n*-hexane is computed to be about 134 cm^{-1}, the following values being used; f=0.316 (the value at 170°C); ν=42000 cm^{-1} (the absorption maximum at 170°C); n=1.438 (the refractive index of *n*-hexane[48] at 42000 cm^{-1}); a=5 Å (as the radius a of the molecule, the round value of the half length of the long molecular axis of biphenyl along which the transition is polarized was provisionally taken by consulting the study by Lippert[49] on *p,p'*-disubstituted stilbenes, although this evaluation is inevitably still somewhat arbitrary).

This calculated value of $\Delta\nu$ may approximately apply to the inferred position of the maximum at 20°C and also to the case where the solvent is *n*-heptane instead of *n*-hexane. Accordingly, being corrected for this solvent effect, the wave number of the position of the maximum of the conjugation band of biphenyl in the vapor state, which is to be compared with the corresponding ones in the spectra of the solutions of biphenyl in *n*-hexane and in *n*-heptane, is evaluated to be 41866 cm^{-1} (at 170°C) or 41966 cm^{-1} (at 20°C).

47) N. D. Coggeshall and A. Pozefsky, *J. Chem. Phys.*, **19**, 980 (1951).
48) J. L. Lauer, ibid., **16**, 612 (1948).
49) E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955).
50) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).

Application of Calculation

On the basis of the above considerations, from the observed positions of the absorption maxima in the solution spectra and the positions in the vapor spectra corrected for the solvent effect, the respectively corresponding values of ΔE_A can be evaluated according to the assumption that ΔE_A varies linearly with μ_A from ΔE_L [1.482$(-\beta)$] for ν_L (40080 or 39841 cm^{-1}) to ΔE_S [2$(-\beta)$] for ν_S (48000 cm^{-1}). Consequently, the corresponding values of μ, θ, R and $R.E.$ can be evaluated in turn. The results are summarized in Table III.

It is shown that the values calculated for the interplanar angles in the most probable conformations of biphenyl in the solution state and in the vapor state are about 20° and about 40~43°, respectively. These values coincide fairly well with those estimated by other workers on different grounds. Thus, Bastiansen[50] deduced the value of 45±10° for the angle in the vapor state from the result of his study by the electron diffraction sector method. This value agrees almost completely with the present one. On the other hand, Samoilov and Dyatkina[51] inferred the value to be about 30° from calculations of resonance energy and steric repulsion energy between the nearest hydrogen atoms by the molecular orbital method. Recently, Adrian[52] concluded, from calculations somewhat similar to those by Samoilov and Dyatkina, that the angle is probably between 20° and 30°. In addition, calculations by Coulson and Longuet-Higgins[53] are said to indicate that

51) S. Samoilov and M. Dyatkina, *Zhur. Fiz. Khim.*, **22**, 1294 (1948); *Chem. Abstr.*, **43**, 2606 (1949).
52) F. J. Adrian, *J. Chem., Phys.*, **28**, 608 (1958).
53) C. A. Coulson, presented at a Conference on Quantum-Mechanical Methods in Valence Theory, Washington, 1951. (According to Refs. 6 and 52.)

the decrease in repulsion energy between the ortho-hydrogen atoms and the decrease in resonance energy resulting from non-planarity are practically balanced for interplanar angles of up to about 20°. All these values are compatible with the values calculated here for the solution state.

Summary

1) The ultraviolet absorption spectra of biphenyl in the crystalline state, in the solution state, and in the vapor state have been discussed in detail.

2) The relation between the position of conjugation band in the spectra of biphenyl and the spatial configuration of the molecule has been clarified by calculations based on the simple LCAO molecular orbital method.

3) By using the results of the calculations, it has been inferred from the analysis of the absorption spectra that the angles between the planes of the two benzene rings in the most probable conformations of biphenyl in the solution state and in the vapor state are about 20° and about 40~43°, respectively. These values coincide fairly well with the values estimated by other workers on different grounds.

The author thanks Professor Kengo Shiomi for his encouragement and for reading the manuscript, Professor Osamu Simamura for his encouragement, and Dr. Yoshiya Kanda of Kyushu University for helpful advice and especially for drawing his attention to Dale's papers which furnished one of the important bases for the present work.

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Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. II. o-Alkyl- and o,o'-Dialkylbiphenyls

By Hiroshi SUZUKI

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In the preceding part[1] of this series the relation between the ultraviolet absorption spectra and the most probable spatial configurations of biphenyl in the various states has been discussed in detail on the basis of the calculation carried out by the simple LCAO molecular orbital method. In the present part, the same method is applied to some ortho-alkyl substituted biphenyl derivatives, and the relation between the spectra and the most probable spatial configurations of these compounds is discussed.

It is well known that atrop-isomerism occurs when two or more, especially when all, of the four ortho hydrogen atoms in biphenyl are replaced by larger atoms or groups. This phenomenon is explained as being due to steric hindrance caused by the substituents which prevents rotation about the central 1—1' bond, namely the co-annular bond, in the biphenyl derivatives. Therefore, the most probable configurations of these compounds must be non-coplanar.

This inference is supported by information from the electronic absorption spectroscopy. Thus, for example, the spectrum of bimesityl does not exhibit the conjugation band characteristic of biphenyl-type compounds, but is closely similar to the sum of the spectra of two mesitylene molecules[2]. This fact is considered to indicate that the twist of the co-annular bond is large enough to eliminate almost completely the π—π interaction across the

1) H. Suzuki, This Bulletin, **32**, 1340 (1959).

2) (a) L. W. Pickett, G. F. Walter and H. France, *J. Am. Chem. Soc.*, **58**, 2296 (1936). (b) M. T. O'Shaughnessy and W. H. Rodebush, ibid., **62**, 2906 (1940). (c) E. Marcus, W. M. Lauer and R. T. Arnold, ibid., **80**, 3742 (1958).

bond in this compound. That is, it is inferred that the two benzene rings in this compound are almost perpendicularly oriented, as suggested by Guy by means of calculations of the energy associated with the tortion about the central linkage in 2, 2', 6, 6'-tetramethylbiphenyl[3].

In either *o*- or *o*, *o*'-substituted biphenyls, the substituents do not confer, unless they are exceptionally large, measurable optical stability on the rotational enantiomorphs at room temperature[4], but contrariwise, they affect markedly the spectral feature. Thus, for example, the conjugation band of *o*-methylbiphenyl is at a considerably shorter wavelength and of considerably lower intensity than that of biphenyl. This hypsochromic shift is believed to indicate that the interplanar angle θ, i. e. the angle of twist of the co-annular bond, in the most probable spatial configuration of *o*-methylbiphenyl is considerably larger than the corresponding one of biphenyl itself. Further, the spectrum of *o*, *o*'-dimethylbiphenyl exhibits no distinct maximum of the conjugation band, but exhibits only an inflection at a further shorter wavelength than the position of the conjugation band of *o*-methylbiphenyl (Fig. 1.).

It is to be noted here that the effect of the substituents upon the spectra of these biphenyl derivatives must include not only the hypsochromic effect due to steric interference of the substituents, but also the electronic (probably bathochromic) effect of the substituents. As is seen in Fig. 1, the absorption maximum of the conjugation band of *p*, *p*'-dimethylbiphenyl

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF BIPHENYL AND ALKYLBIPHENYLS

Compound	Solvent	Conjugation band		Ref.
		λ_{max}	ε	
Biphenyl	E	247.7	18050	1)
	Hp	247.0	16450	1)
p-Methyl-	E	253	13300	5)
o-Methyl-	E	235	10500	6)
	E	ca. 237	9960	a
	E	ca. 235		8)
	Cy	ca. 235		8)
	Hp	235	10000	7)
o-Ethyl-	E	233	10500	6)
o-*n*-Propyl-	E	233	10000	6)
o-Isopropyl-	E	233	11000	6)
o-*n*-Butyl-	E	233	10500	6)
p, *p*'-Dimethyl-	E	255.6	20500	a
	E	ca. 260	20000	9)
	Hp	255.2	21200	a
	Hx	256	21400	10)
o, *o*'-Dimethyl-	E	(ca. 227)	6800	11)
	E	(228～229)	(6000～6500)	a
p, *p*'-Diethyl-	E	256.5	22500	12)
p, *p*'-Diisopropyl-	E	256.5	23500	12)
o, *o*'-Diethyl-	E	(ca. 277)	6000	12)
o, *o*'-Diisopropyl-	E	(ca. 277)	5500	12)
o, *o*'-Di-*tirt*-butyl-	E	No conjugation band		12)
Bimesityl		No conjugation band		2)

Solvent: E, ethanol; Hp, *n*-heptane; Cy, cyclohexane; Hx, *n*-hexane.
Wavelengths (mμ) in parentheses denote inflections.
Ref. a refers to the present work.

3) J. Guy, *J. chim. phys.*, **46**, 469 (1949).
4) R. Adams and H. C. Yuan, *Chem. Revs.*, **12**, 261 (1933).
5) The Chemical Society of Japan, "Jikken Kagaku Koza" Vol. 1, Maruzen Co., Ltd., Tokyo (1957), p. 191 (K. Hirayama).
6) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, **1955**, 3776.
7) H. Suzuki, This Bulletin, **27**, 597 (1954).
8) R. A. Friedel, M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **70**, 199 (1948).
9) B. Williamson and W. H. Rodebush, ibid., **63**, 3018 (1941).
10) R. A. Friedel and M. Orchin, "Ultraviolet Absorption of Aromatic Compounds", John Wiley & Sons, Inc., New York (1951).
11) G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner and G. R. Bird, *J. Chem. Soc.*, **1954**, 131.
12) P. M. Everitt, D. M. Hall and E. E. Turner, ibid., **1956**, 2286.

from which the steric interference of the substituents is absent is at a considerably longer wavelengths as compared with the corresponding one of biphenyl. This bathochromic displacement of the band is probably due to the hyperconjugation effect of methyl groups. The similar bathochromic effect due to hyperconjugation must operate also in the spectra of ortho-substituted biphenyl derivatives such as *o*-methyl- and *o*, *o*'-dimethylbiphenyl. Accordingly, in order to clarify the relation between the spectra and the spatial configurations of *o*-alkyl- and *o*, *o*-dialkylbiphenyls, it is necessary to make allowance for the electronic bathochromic effect of the substituents.

Spectra of Alkylbiphenyls

The data of the ultraviolet absorption spectra of some alkylbiphenyls are summarized in Table I, in which that of biphenyl is included for comparison. Of the spectra measured by the present author, those of biphenyl and of *p*, *p*'-dimethylbiphenyl were measured with a Cary recording spectrophotometer Model 14 and those of *o*-methyl- and of *o*, *o*'-dimethylbiphenyl with a Beckman quartz spectrophotometer Model DU. These spectra are shown also in Fig. 1[13].

***o*-Alkylbiphenyls.**—The absorption maximum of the conjugation band of *p*-methylbiphenyl is at 253 mμ. The bathochromic effect due to the hyperconjugation effect of a *p*-methyl group and that of an *o*-methyl group are considered to be approximately of the same magnitude, as supported by the comparison of the results of calculations of the energy levels in *p*-terphenyl and in *o*-terphenyl, which will be reported in Part IV of this series.

Accordingly, if the steric effect of the ortho methyl substituent were absent, *o*-methylbiphenyl would exhibit the conjugation band at approximately the same position as that of the *p*-isomer. Hence *p*-methylbiphenyl may reasonably be taken as the longer-wavelength-side reference compound in this case.

It was reported in the preceding part that the value of the parameter μ' in the $\pi-\pi$ resonance integral $\mu'\beta$ for the 1–1' bond in biphenyl in solution is 0.780 and that the corresponding calculated transition energy ΔE_A is 1.523 $(-\beta)$ (cf. Table III in Ref. 1). From the above consideration, these values are assumed here to correspond approximately to the position of the maximum of the conjugation band of *p*-methylbiphenyl. That is, the values of ΔE_L and of ν_L in the present treatment of *o*-methylbiphenyl are assumed to be 1.523 $(-\beta)$ and 39526 cm^{-1} (253 mμ), respectively.

On the other hand, as the value of ν_S corresponding to ΔE_S $[2(-\beta)]$ when μ' is 0, analogously to the choice of the "center of gravity of singlets" 48000 cm^{-1} of benzene[14] in the case of biphenyl itself[1], the corresponding value of toluene may be taken here.

In Table II, a collection of the relevant data of the spectra of benzene and of several alkylbenzenes is assembled. In this table also the data of *m*-xylene and of mesitylene which are not needed in the present part are conveniently included for the sake of reference in the later parts (probably VIII and XI) of this series.

It is seen in Table II that each of the bands of toluene is at a longer wavelength by about 5 mμ than the corresponding band of benzene. Therefore, as the value of toluene corresponding to the center of gravity of singlets 48000 cm^{-1} (208.3 mμ) of benzene, the value of 46882 cm^{-1} (213.3 mμ) may be taken. Accordingly, the value of ν_S is assumed here to be 46882 cm^{-1}.

In this manner, the allowance for the electronic bathochromic effect of the substituent is made by the choice of the

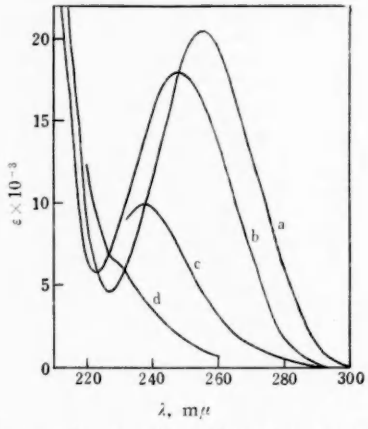

Fig. 1. The ultraviolet absorption spectra of biphenyl and of methylbipenyls in ethanol.
a: *p*, *p*'-Dimethylbiphenyl. b: Biphenyl.
c: *o*-Methylbiphenyl. *d*: *o*, *o*'-Dimethylbiphenyl.

13) The author is indebted to Dr. Makoto Takahashi for a generous supply of the sample of *p*, *p*'-dimethylbiphenyl. Preparations of *o*-methyl- and of *o*,*o*'-dimethylbipheyl wer reported in Ref. 7.

14) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

TABLE II-1. ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE AND ALKYLBENZENES (in *n*-heptane)[15]

Compound	Allowed transition			Forbidden transition		
	λ_{max}, mμ	ε	f	λ_{max}, mμ	ε	f
Benzene	183.5	46000	0.69	195.0	6900	0.10
Toluene	188.5	55000	0.97	200.0	8100	0.12
Ethylbenzene	189.0	57000	1.00	200.0	7400	0.11
m-Xylene	193.0	76000	1.28	203.0	10500	0.18

TABLE II-2. ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE AND ALKYLBENZENES

Compound	Approx. center of band[16] (in *n*-hexane)		O-O band[17] (vapor)	O-O band[18]
	λ, mμ	ε	λ_{max}, mμ	λ_{max}, mμ
Benzene	255	230	262.54	262.46
Toluene	261	300	266.78	266.75
Ethylbenzene	261	220		266.43
n-Propylbenzene	261	245		266.52
Isopropylbenzene				265.87
n-Butylbenzene	260	235		266.63
m-Xylene	266	400		
Mesitylene	266	305	274.06	

references for correlation between the observed position of the conjugation band and the calculated transition energy. Thus, quite analogously to the treatment in the preceding part, the value of the transition energy ΔE_A corresponding to the wave number of the absorption maximum of the conjugation band of *o*-methylbiphenyl can be computed (cf. Eq. 8 in Ref. 1). In this case, it is assumed that ΔE_A varies linearly with ν_A in the range of ΔE_L [1.523 $(-\beta)$] to ΔE_S [2$(-\beta)$]. By the way, ΔE_L and ΔE_S correspond to ν_L (39526 cm^{-1}) and ν_S (46882 cm^{-1}), respectively. Then, one can obtain the corresponding values of μ, θ, R, etc. in turn according to the relation between ΔE_A and μ (cf. Table I in Ref. 1), and to the relation between μ and θ as well as R (the length of the 1–1′ bond) (cf. Eqs. 1–7 in Ref. 1), which were postulated in the preceding part.

The absorption maxima of ethyl-, *n*-propyl- and *n*-butylbenzene are located at about the same wavelength, 260~261 mμ, as that of toluene. On the other hand, *o*-ethyl- *o*-*n*-propyl-, *o*-isopropyl-, and *o*-*n*-butylbiphenyl all exhibit the maxima of the conjugation bands at about the same wavelength, 233 mμ. Hence it is obvious that these *o*-alkylbiphenyls can be approximately treated also by application of the relation between ΔE_A and ν_A assumed above for the case of the *o*-methyl analogue.

o, o′-Dialkylbiphenyls. — The absorption spectra of *o*, *o*′-dimethyl-, *o*, *o*′-diethyl-, and *o*, *o*′-diisopropylbiphenyl are markedly different from those of the corresponding *o*-monoalkylbiphenyls. Each of the spectra of these *o*, *o*′-dialkylbiphenyls shows no distinct absorption maximum of the conjugation band, but merely an inflection at about 227 mμ, which is regarded as the vestigial or submerged conjugation band. According to Everitt and his coworkers[12], the spectra of these *o*, *o*′-dialkylbiphenyls exhibit feeble bands at about 263.5 mμ and at about 270~271 mμ (the molar extinction coefficients are lower than 1000) in addition to the vestigial conjugation band mentioned above. These feeble bands are believed to correspond to the "hidden transition" in biphenyl[19], and this revelation is probably due to the marked hypsochromic shift and the reduction in the intensity of the conjugation band caused by larger deviation from coplanarity of the configuration in these sterically hindered biphenyl derivatives, as compared with biphenyl itself.

In order to infer the most probable spatial configurations of these *o*, *o*′-dialkylbiphenyls by application of the present

15) J. R. Platt and H. B. Klevens, *Chem. Revs*, **41**, 301 (1947).
16) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy", 2nd Ed., Edward Arnold Publishers, Ltd., London (1957), p. 134.
17) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).
18) W. West, "Chemical Applications of Spectroscopy" (Technique of Organic Chemistry IX), Interscience Publishers., Inc., New York (1956), p. 677 (F. A. Matsen).
19) A. Wenzel, *J. Chem. Phys.*, **21**, 403 (1953). See also Ref. 1.

TABLE III. RESULTS OF CALCULATION

Biphenyl derivative	λ_{max}, mμ	ν_A, cm^{-1}	ΔE_A, $-\beta$	μ	θ	R, Å
o-Methyl-	235	42553	1.719	0.438	58°	1.508
o-Ethyl-, *o*-*n*-propyl, *o*-isopropyl-, *o*-*n*-butyl-	233	42918	1.743	0.399	60.7	1.5105
o,*o*'-Dimethyl-	(227)	44053	1.826	0.267	70	1.5193
o,*o*'-Diethyl-, *o*,*o*'-diisopropyl-	(227)	44053	1.829	0.262	70.3	1.5195

method, allowance for the electronic bathochromic effects of the substituents is made analogously to the case of *o*-monoalkylbiphenyls by choice of the references for correlation between the calculated transition energy and the observed position of the conjugation band. Thus, as ν_L corresponding to ΔE_L 1.523 $(-\beta)$, the wave number 39124 cm^{-1} (255.6 mμ) of the maximum of the conjugation band of *p*,*p*'-dimethylbiphenyl is taken in the case of *o*,*o*'-dimethylbiphenyl, and the wave number 38986 cm^{-1} (256.5 mμ) of the maxima of the conjugation bands of *p*,*p*'-diethyl- and *p*,*p*'-diisopropylbiphenyl is taken in the case of the corresponding *o*,*o*'-isomers. On the other hand, as ν_S corresponding to ΔE_S $2(-\beta)$, the value of monoalkylbenzene 46882 cm^{-1} (213.3 mμ) corresponding to the center of gravity of singlets of benzene is taken, quite similarly to the case of *o*-monoalkylbiphenyls.

Results of Calculations and Discussion

The results of the calculations are shown in Table III. The calculated value of the angle of twist in *o*-methylbiphenyl is in considerably good agreement with the value 62° deduced from the scale model in which the length of the 1–1' bond is 1.51 Å, the lengths of C_6H_5–H bond and of the C_6H_5–CH_3 bond are 1.08 and 1.54 Å, respectively, the radii of hydrogen atom and of methyl group are 0.9 and 2.0 Å, respectively, and an ortho hydrogen atom just touches the ortho methyl group.

It is noteworthy that the values of the angle of twist in *o*-ethyl-, *o*-*n*-propyl-, *o*-isopropyl-, and *o*-*n*-butylbiphenyl are equal to each other, and that they are merely slightly larger than that in the methyl analogue. This fact may be considered to indicate that all but the methylene group attached directly to the phenyl ring can adopt conformations such that they cause little or no additional interference, as suggested already by Braude and Forbes[6].

The calculated value of the interplanar angle in *o*,*o*'-dimethylbiphenyl is eventually closely similar to the value estimated in the earlier paper[7], 70.5°. Therefore, the discussion in the earlier paper may apply also to the present result. Thus, this value 70° of the interplanar angle in *o*,*o*'-dimethylbiphenyl coincides almost exactly with the corresponding value, 70.6°, found for 2,2'-dimethylbenzidine dihydrochloride by the X-ray crystal analysis[20], and it is inferred that the preferred configuration of the former is similar to the configuration of the latter which has been found to have the two ortho methyl groups in the *cis*-disposition. This inference of the *cis*-configuration of *o*,*o*'-dimethylbiphenyl seems to be supported also by the fact that the interplanar angle in gaseous 2,2'-dichlorobiphenyl found by the electron diffraction method[21] and that in crystalline 2,2'-dichlorobenzidine found by the X-ray crystal analysis[22] are 74° and 72°, respectively, and that both these compounds have been found to have *cis*-configurations.

If the molecule of *o*,*o*'-dimethylbiphenyl assumed the *trans*-configuration in which the ortho hydrogen atoms just contact with the ortho methyl groups, the configuration of the biphenyl skeleton would be similar to that in *o*-methylbiphenyl, and consequently *o*,*o*'-dimethylbiphenyl would show a closely similar spectrum to that of *o*-methylbiphenyl. In fact it is not so. Thus, as already mentioned, the hypsochromic shift of the conjugation band is observed to be markedly larger in the spectrum of *o*,*o*'-dimethylbiphenyl than in that of *o*-methylbiphenyl.

This fact has been interpreted by Braude and Forbes[6] as follows: "The hypsochromic shift from 2500 to 2350 Å due to one *o*-methyl substituent actually corresponds to an increase in transition energy of 7 kcal./mol., which is the amount by which the energy level of the electronic excited

20) (a) F. Fowwether and A. Hargreaves, *Acta Cryst.*, **3**, 81 (1950); *Chem. Abstr.*, **44**, 7118 (1950). (b) A. Hargreaves and W. H. Taylor, *J. Sci. Instruments*, **18**, 138 (1941); *Chem. Abstr.*, **35**, 7261 (1941).
21) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).
22) D. L. Smare, *Acta Cryst.*, **1**, 150 (1948); *Chem. Abstr.* **42**, 8045 (1948).

state has been raised relative to that of the ground state and it is obviously reasonable that the effect of two such substituents should be about twice as great". It seems that they have attributed the hypsochromic shift, viz. an increase in transition energy, to an increase in the difference between the steric repulsion energy in the electronic excited state and that in the ground state.

However, as mentioned already in the preceding part[1] of this series, since the transition is considered to be an electron jump without change in nuclear configuration according to the Franck-Condon principle, the steric repulsion energy in the electronic excited state and that in the ground state must be at least approximately of the same magnitude. Therefore, whereas the steric repulsion energy is a contributing factor to the stability of the molecule and hence to determination of the most probable spatial configuration of the molecule, the electronic transition energy must not depend directly on the steric repulsion energy in the ground state, but on the spatial configuration itself. And further, of course, there should be no direct relation between the electronic transition energy and the height of the energy barrier to rotation about the co-annular bond which depends mainly on the difference between the steric repulsion energy in the coplanar configuration and that in the most probable configuration.

From such considerations, the difference between the spectrum of *o*-methylbiphenyl and that of *o*, *o'*-dimethylbiphenyl should be ascribed to the difference of the most probable spatial configurations of the biphenyl skeleton in these compounds. It is obvious that the interpretation by Braude and his coworker is quite unreasonable.

o, *o'*-Diethyl- and *o*, *o'*-diisopropylbiphenyl are inferred to have configurations similar to that of *o*, *o'*-dimethylbiphenyl, although the estimation of the interplanar angle in these compounds is inevitably somewhat uncertain since the conjugation bands of these compounds are vestigial, the positions of the maxima of which can not accurately be determined.

o, *o'*-Di-*tert*-butylbiphenyl exhibits no trace of a discrete conjugation band. This fact may be considered to indicate that the interplanar angle in this compound is so large owing to the bulkiness of the substituents that the $\pi-\pi$ interaction across the co-annular bond is almost completely eliminated.

23) W. Theilacker and W. Ozegowski, *Ber.*, **73**, 33 (1940).

Relation of Spatial Configurations with Other Properties

The difference of the spatial configurations of the compounds must undoubtedly affect also certain physical and chemical properties of the compounds besides the electronic absorption spectra. Accordingly, the spatial configurations of the biphenyls inferred above on the basis of the absorption spectra may be correlated with various other properties of the compounds. A few examples are given below.

Theilacker and Ozegowsky[23] found that 2, 2'-dimethyl-4, 4'-biphenylene-bis-diphenylmethyl has properties closely similar to those of the 2, 2', 6, 6'-tetrachloro analogue which is known to be a true biradical[24]. In addition, Müller and Hertel[25] concluded from the result of measurement of the magnetic susceptibility that this 2, 2'-dimethyl compound is paramagnetic and hence a true biradical in contrast to its parent compound, Chichibabin's hydrocarbon, which had been found to be completely diamagnetic and not a biradical[26]. Although the latter compound was found afterwards by application of the paramagnetic resonance absorption method to contain about 4% of the biradical form in solution in benzene[27], it may be safe to state that in the equilibrium between the diphenoquinone form and the biradical form the latter form is more favorable in the 2, 2'-dimethyl compound than in the parent compound, and that this fact is to be related to the reduced $\pi-\pi$ interaction across the co-annular bond in the former compound as compared with the latter compound.

According to Sherwood and Calvin[28], in *p*-amino-*p'*-nitrobiphenyl the *p'*-nitro group exerts a marked effect upon the basicity of the *p*-amino group and this effect is diminished by ortho substitution by two methyl groups. This effect of ortho methyl groups has been ascribed to the blocking of nitro-amino resonance by the forced non-coplanarity of the configuration of the biphenyl skeleton.

Castro, Andrews and Keefer[29] recently measured the equilibrium constants and the heats of formation of 1 : 1 complexes of a series of methylbiphenyls with 1, 3, 5-trinitrobenzene. According to their results, whereas the complexes increase in stability as the number of *p*-methyl substituents on the biphenyl nucleus is increased, the complex stability decreases in the order

24) E. Müller, ibid., **72**, 2063 (1939).
25) E. Müller and E. Hertel, *Ann.*, **555**, 157 (1944).
26) E. Müller and I. Müller-Rodloff, ibid., **517**, 134 (1935).
27) C. A. Hutchison, Jr., A. Kowalsky, R. C. Pastor and G. W. Wheland, *J. Chem. Phys.*, **20**, 1485 (1952).
28) D. W. Sherwood and M. Calvin, *J. Am. Chem. Soc.*, **64**, 1350 (1942).
29) C. E. Castro, L. J. Andrews and R. M. Keefer, ibid., **80**, 2322 (1958).

biphenyl > *o*-methylbiphenyl > *o*, *o*'-dimethylbiphenyl > bimesityl, as the number of *o*-methyl substituents is increased. This fact is indicative of the dependence of the complex stability on the factors which prevent coplanarity of the two benzene rings in the biphenyl derivatives, and supports the present conclusion that the degree of deviation from planarity of the configuration of biphenyl skeleton increases as the number of *o*-methyl substituents is increased.

Furthermore, Brownstein[30] measured the nuclear magnetic resonance absorption spectra of some 2-halo- and 4-halobiphenyls and attributed shifts in proton resonance absorption toward a higher field observed for some of the protons in 2-halobiphenyls to steric effects of the halogen upon the ortho protons of the unsubstituted benzene ring. In addition, he explained the melting points of these compounds by the twisting of the benzene rings as the size of the 2-substituent is increased. Thus, whereas a heightening of melting point is observed with increasing molecular weight for the 4-halobiphenyl as would be expected, the melting point of the 2-halobiphenyl is lowered as the molecular weight increases. This was believed to be caused by the decreasing symmetry of the molecule as the benzene rings are twisted further out of plane by the steric effect of the *o*-substituent.

Although the melting point is a very complex property, it may be sure that the spatial configuration of the molecule is an important factor to govern the melting point. A somewhat similar phenomenon to the one mentioned above is observed in the series of methylbiphenyls. Thus, whereas the melting points of biphenyl and of *p*-methylbiphenyl are 69 and 49~50°C (47~48°C), respectively, *o*-methylbiphenyl is liquid at room temperature. In addition, whereas the melting point of *p*, *p*'-dimethylbiphenyl is 125°C (121°C), that of the *o*, *o*'-isomer is 18°C. (Data of the melting points are according to Dictionary edited by Heilbron[31]). The fact that the melting point of the *o*-isomer is invariably markedly lower than that of the corresponding *p*-isomer may be at least partly due to the non-planarity of the configuration of the *o*-isomer.

30) S. Brownstein, ibid., **80**, 2057 (1958).

Summary

The method described in the preceding part of this series has been applied with allowance for the electronic bathochromic effect of the substituents to *o*-alkyl- and *o*, *o*'-dialkylbiphenyls, and the relation between the ultraviolet absorption spectra and the most probable spatial configurations of these compounds has been clarified, resulting in the conclusion that the interplanar angle in *o*-methylbiphenyl as well as its analogues is about 60° and that *o*, *o*'-dimethylbiphenyl as well as its analogues has the *cis*-configuration in which the interplanar angle is about 70°.

On the basis of the result, the interpretation by Braude and Forbes of the spectra of *o*-methyl- and *o*, *o*'-dimethylbiphenyl has been criticized.

In addition, the inferred spatial configurations of these biphenyl derivatives have been correlated with some physical and chemical properties of these and some related compounds.

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31) I. Heilbron, "Dictionary of Organic Compounds", Oxford University Presss, Inc., New York (1953).

Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. III. o,o'-Bridged Biphenyls

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The method developed in the earlier parts[1,2] of this series is applied to some *o,o'*-bridged biphenyls, and the relation between the ultraviolet absorption spectra and the spatial configurations of these compounds is discussed.

A collection of the data of the spectra of some *o,o'*-bridged biphenyls is assembled in Table I.

o,o'-One-atom-bridged and Two-atom-bridged Biphenyls

The spectra of fluorene and of 9,10-dihydrophenanthrene exhibit besides the intense bands at about 260 mμ lower bands at about 300 mμ. The former bands are probably the conjugation bands characteristic of the biphenyl-type compounds. The

TALBE I. ULTRAVIOLET ABSORPTION SPECTRA OF *o,o'*-BRIDGED BIPHENYLS

Entry No.	Compound	Solvent	Conjugation band		Ref.
			λ_{max}, mμ	ε	
1	Fluorene	Hp	261.5*	18900	a
		E	ca. 260*	19000	3)
2	9,10-Dihydrophenanthrene	Hx	263.5	18000	4)
		E	264	17000	4)
3	4,5-Methylene-9,10-dihydrophenanthrene	E	ca. 272	ca. 18500	5)
o,o'-Three-atom-bridged biphenyls					
4	2,7-Dihydro-3,4-5,6-dibenzoxepin	Hx	250	16500	4)
5	3,4-5,6-Dibenzocyclohepta-3,5-diene-1-carboxylic acid	E	249	15300	6)
6	6,6-Dicarbethoxydibenzo-[a,c][1,3]-cycloheptadiene	E	249	16980	7)
7	Methyl 3,4-5,6-dibenzocyclohepta-3,5-diene-1-carboxylate	E	248.5	15500	6)
8	1-Hydroxymethyl-3,4-5,6-dibenzocyclohepta-3,5-diene	E	248.5	15400	6)
9	2,7-Dihydro-3,4-5,6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide	W	248	15000	4)
o,o'-Four-atom-bridged biphenyls					
10	Ethyl 4,5-6,7-dibenzocycloocta-4,6-diene-1,1,2,2-tetracarboxylate	E	239.5	13100	6)
11	Methyl 4,5-6,7-dibenzocycloocta-4,6-diene-1,2-dicarboxylate	E	236.5	12700	6)

Solvent: E, ethanol; Hp, *n*-heptane; Hx, *n*-hexane; W, water.
* The most intense maximum of fine structure.
Ref. a refers to the present work (cf. Table II and Fig. 1).

1) H. Suzuki, This Bulletin, **32**, 1340 (1959).
2) H. Suzuki, ibid., **32**, 1350 (1959).
3) W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937).
4) G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, **1952**, 854.
5) R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941).
6) G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladburg, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, **1955**, 2708.
7) D. C. Iffland and H. Siegel, *J. Am. Chem. Soc.*, **80**, 1947 (1958).

latter, which are absent from biphenyl, are difficult to interpret. Braude[8,9] seems to have attempted to explain these feeble bands by means of an assumption of C–C hyperconjugative interaction of the two benzene rings through the methylene bridge. Perhaps these bands may be considered to correspond to the "hidden transition" in biphenyl[10].

The spectrum of fluorene and that of 9,10-dihydrophenanthrene resemble each other considerably on the whole[11]. However, while the latter shows no fine structure, the former shows a remarkably well-resolved fine structure (Table II and Fig. 1). This may be related to the fact that fluorene has probably a strained or forced coplanar or near-coplanar configuration.

TABLE II. THE ULTRAVIOLET ABSORPTION SPECTRUM OF FLUORENE IN *n*-HEPTANE MEASURED ON A CARY RECORDING SPECTROPHOTOMETER MODEL 14 M-50 (cf. Fig. 1)

Conjugation band

λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε
300.3	10070	(277.4)	8350	226.5	5680
293.6	5020	272.2	13050	220.4	16250
288.9	6190	264.2	18720	208.5	42500
		261.5	18900	204.3	44500
		(255.5)	16630		

Wavelengths in parentheses denote inflections.

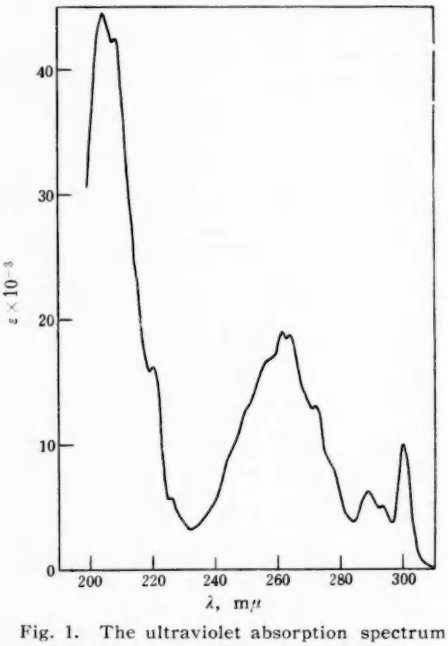

Fig. 1. The ultraviolet absorption spectrum of fluorene in *n*-heptane (cf. Table II).

The conjugation band of fluorene is at considerably longer wavelengths than that of biphenyl. This bathochromic shift of the band may be partly due to the forced coplanarity or near-coplanarity of the molecular configuration of fluorene, and partly to the hyperconjugation of the methylene group. When the relation postulated for biphenyl[1] between the calculated electronic transition energy ΔE_A and the observed position ν_A (in wave number) of the maximum of the conjugation band is provisionally applied without allowance for the bathochromic (hyperconjugation) effect of the substituent to fluorene, the value of the parameter μ in the π—π resonance integral $\mu\beta$ for the co-annular bond in fluorene is estimated to be about 1.060 from the position 261.5 mμ (in *n*-heptane) of the most intense maximum of the conjugation band. This value is to be compared with the corresponding value 0.780 or 0.762 for biphenyl in solution, although this value for fluorene should be considered as a measure of the degree of "conjugation" in fluorene including hyperconjugation of the methylene group as well as intrinsic conjugation which depends on the spatial configuration of the biphenyl skeleton. The fact that the degree of conjugation in fluorene is considerably larger than in biphenyl may explain at least partly the extraordinarily larger reactivity of fluorene as compared with biphenyl in some kinds of reactions. A few examples are given below.

The reactivity of fluorene to nitration is much higher than that of biphenyl. Thus, while the "partial rate factor" (the rate constant of separate nuclear position of the compound relative to one nuclear position of benzene being taken as unity) at *p*-position and that at *o*-position in biphenyl are 38 and 41, respectively[12], or 11.0 and 18.5, respectively[13], the values at the corresponding positions (i.e. the 2- or 7- and the 4- or 5-positions) in fluorene are 2040 and 944, respectively[14].

8) E. A. Braude, *J. Chem. Soc.*, **1949**, 1902.
9) E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., New York (1955), p. 154 ff. (E. A. Braude).
10) A. Wenzel, *J. Chem. Phys.*, **21**, 403 (1953). See also Ref. 1.
11) R. N. Jones, *J. Am. Chem. Soc.* **67**, 2127 (1945).
12) O. Simamura and Y. Mizuno, This Bulletin, **30**, 196 (1957).
13) P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, **1957**, 3004.
14) M. J. S. Dewar and D. S. Urch, ibid., **1958**, 3079.

Berliner and Shieh[15] have correlated the rate constants of solvolysis of α-arylethyl chlorides with the atom localization energies calculated by Dewar and others for the aryl radicals, and found that the reactivity of 2-fluorenyl compound is extraordinarily higher than expectation.

In addition, Sandin and coworkers[16] have compared the carcinogenic activities of 2-acetylaminofluorene, 4-acetylaminobiphenyl, and their related compounds, and found the fact that 2-acetylaminofluorene has a much higher activity as compared with 4-acetylaminobiphenyl and especially its *o*-methyl substituted derivatives. They have ascribed this fact to the greater planarity of the configuration of the biphenyl skeleton in 2-acetylaminofluorene than in the other compounds.

The interplanar angle in 9,10-dihydrophenanthrene has been estimated by Beaven and coworkers[1] to be about 20° by means of a model in which the saturated carbon atoms maintain their tetrahedral valency angle. Accordingly the bathochromic displacement of the conjugation band of this compound relative to that of biphenyl may be due mainly to the normal electronic substituent effect (probably hyperconjugation effect) of the alkyl group.

The maximum of the conjugation band of 4,5-methylene-9,10-dihydrophenanthrene is at even longer wavelengths than those of fluorene and 9,10-dihydrophenanthrene. In this compound the conflicting steric requirements of the two bridges would appear to be most favorably compromised in an approximately planar configuration. Accordingly the bathochromic shift of the conjugation band of this compound relative to those of fluorene and of 9,10-dihydrophenanthrene may be ascribed partly to the planarity or nearer-planarity of the configuration, and partly to the electronic substituent effect of the additional dimethylene or methylene bridge.

o,o'-Three-atom-bridged and Four-atom-bridged Biphenyls

Each of the spectra of the compounds in which the *o,o'*-positions of biphenyl are bridged by a 7-membered ring (which are subsequently referred to as the *o,o'*-three-atom-bridged biphenyls) (entries 4—9, Table I) shows the conjugation band at considerably shorter wavelengths than those of fluorene and of 9,10-dihydrophenanthrene. The corresponding band of each of the compounds in which the *o,o'*-positions of biphenyl are bridged by an 8-membered ring (the *o,o'*-four-atom-bridged biphenyls, entries 10 and 11) is further shifted toward shorter wavelengths.

These *o,o'*-three-atom-bridged and four-atom-bridged biphenyls are considered to have non-planar configurations. Accordingly, the hypsochromic displacements of the conjugation band observed in these compounds with respect to fluorene or 9,10-dihydrophenanthrene are probably ascribed to the non-planarity of the configurations, and therefore, their configurations may be inferred from their spectra by application of the method described in the earlier parts of this series.

In application of the method to these compounds, 9,10-dihydrophenanthrene is taken as the longer-wavelength-side reference compound. The justification for taking this compound rather than fluorene as the reference compound is that this makes a pertinent allowance for the bathochromic effect of two methylene groups attached at the *o*- and the *o'*-positions of biphenyl, and further justification is found in the fact that the molecule of fluorene is presumed to contain a considerably large strain.

The previously assumed relation between the length of the co-annular bond R and the interplanar angle θ (Eqs. 4 and 5 in Part I of this series) may not be pertinent to this case. However, a slight change in the value of R does not substantially affect the calculated value of the interplanar angle θ, as suggested by the results of calculations in the case of terphenyls which will be described in the next part of this series. Hence the relation is applied to the present case for simplification. Then, adopting the value (about 20°) estimated by Beaven and coworkers from the scale model for the interplanar angle in 9,10-dihydrophenanthrene, the corresponding value of R is computed to be 1.4837 Å, and the parameter μ in the $\pi-\pi$ resonance integral $\mu\beta$ for the co-annular bond is evaluated to be 0.801. Consequently, the value of the calculated transition energy $1.5115(-\beta)$, viz. ΔE_L, when μ is 0.801 is assumed to correspond to the wave number 37879 cm^{-1} (264 mμ),

15) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).
16) R. B. Sandin, R. Melley, A. S. Hay, R. N. Jones, E. C. Miller and J. A. Miller, ibid., **74**, 5073 (1952).

viz. ν_L, of the position of the maximum of the conjugation band in the spectrum of 9,10-dihydrophenanthrene in ethanol. (In the present treatment the data of the spectra of the solutions in ethanol are compared in principle.)

As the shorter-wavelength-side reference, quite similarly to the previous treatment of *o*-alkyl- and *o,o'*-dialkylbiphenyls[2], the value of toluene, 46882 cm^{-1} (213.3 $m\mu$), corresponding to the "center of gravity of singlets" of benzene is taken, because the effect of a methylene group upon the positions of the bands of benzene is considered to be approximately of the same magnitude as that of a methyl group (cf. Table II in Part II of this series). That is, the value of 46882 cm^{-1} (viz. ν_S) is assumed to correspond to the value of the calculated transition energy $2(-\beta)$ (viz. ΔE_S) when μ is 0.

On the basis of the above assumptions, the value of ΔE_A, μ, θ, R, etc. for each of the *o,o'*-three-atom-bridged and the *o,o'*-four-atom-bridged biphenyls can be computed by the usual procedure from the position of the conjugation band in its spectrum. The results of calculations are summarized in Table III.

TABLE III. RESULTS OF CALCULATION

Compound	λ_{max} $m\mu$	ν_A cm^{-1}	$\Delta E_A/-\beta$	μ	θ	R Å
o,o'-Three-atom-bridged biphenyls						
4	250	40000	1.627	0.594	44.5°	1.497
5, 6	249	40161	1.635	0.579	46.0	1.498
7, 8	248.5	40241	1.640	0.572	46.7	1.499
9	248	40323	1.644	0.565	47.3	1.499
(Average)	249	40161	1.635	0.579	46.0	1.498
o,o'-Four-atom-bridged biphenyls						
10	239.5	41754	1.722	0.434	58.0	1.508
11	236.5	42283	1.751	0.387	61.5	1.511
(Average)	238	42017	1.736	0.411	59.8	1.510

Compounds are represented by the entry numbers in Table I.

Beaven and coworkers have estimated the interplanar angle in *o,o'*-three-atom-bridged biphenyls as about 50°[4], and that in *o,o'*-four-atom-bridged biphenyls as about 60~65°[6] from models. The values have been computed here to be 44.5~47.3° average, 46°) and 58.0~61.5° (average, 59.8°), respectively, which agree fairly well with the values estimated from models.

From the close similarity between the spectrum of 2,7-dihydro-3,4-5,6-dibenzoxepin (entry 4,Table I)and that of biphenyl Beaven and others[1] have presumed that "in the oxepin the phenyl groups are no less conjugated and hence no less coplanar than in biphenyl", and concluded that "the biphenyl-type spectrum does not provide sure evidence for a coplanar configuration" "since the oxepin can not be coplanar". In addition, the present author considered in the previous paper[17] that the estimation of the value of the interplanar angle in biphenyl as about 50° was supported by this spectral similarity. A common flaw in these considerations is that the bathochromic effect of the substituents was not sufficiently taken into account.

On the other hand, Braude and Forbes[18] have estimated the interplanar angles in ortho-bridged biphenyls and their related compounds by applying the equation $\cos\theta = \varepsilon/\varepsilon_0$, assuming that ε_0 is equal to the molar extinction coefficient of the conjugation band of fluorene, and obtained the following values; 21° for 2,7-dihydro-3,4-5,6-dibenzoxepin (entry 4, Table I), 41° for its *o,o'*-dimethyl derivative, 47° for its *o,o'*-dimethoxy-derivative, and 27° for 2,7-dihydro-3,4-5,6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide (entry 9).

Their equation mentioned above has been assumed to be true on the basis of the hypothesis of transitions from the non-planar ground state to the uniplanar or near-planar excited state, and the starting point of their theory is the assumption that the absorption intensity is determined by the transition probability which is in turn governed mainly by the probability in which the molecule in the ground state assumes the uniplanar or near-planar configuration[19]. However, this probability must be governed by the shape of the potential energy curve for the tortional vibration, and hence mainly by the energy difference between the uniplanar or near-planar configuration and the most probable configuration. In spite of the hypothesis by Braude and others, it seems to be very questionable whether or not there is any direct relation between this probability, namely, the height of the energy barrier to the rotation about the pivot bond and the interplanar angle in the most probable configuration.

Furthermore, according to its basic theory, the equation mentioned above

17) H. Suzuki, This Bulletin, **27**, 597 (1954).
18) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, **1955**, 3776.
19) E. A. Braude and F. Sondheimer, ibid., **1955**, 3754.

should be applied only to the case in which the so-called steric effect of type 1 is exerted, that is, to the case in which a reduction in the intensity of the conjugation band occurs alone without any significant hypsochromic shift. Nevertheless, it is evident that in the spectra of the compounds cited by Braude and Forbes remarkable hypsochromic shifts are involved. The application of the equation to these compounds is, therefore, inconsistent with its basic theory itself.

The introduction of two *o*-methyl groups or of two *o*-methoxyl groups into dihydrodibenzoxepin (entry 4, Table I) causes a remarkable decrease in the intensity of the "biphenyl-type" conjugation band. Considering this effect as being mainly due to the steric effect, Braude and Forbes[18] have stated that the assumption by Beaven and others of an angle of 50° between the benzene rings in the parent oxepin is questionable. Thus, adopting the assumption of Beaven and others, since the benzene rings in this compound are already at an angle of about 50°, the introduction of the *o*-substituents should have no steric consequences. On the other hand, Beaven and others[4] have attempted to explain this effect of the substituents by electronic interaction between the substituents and the separate benzene rings to which they are attached.

However, in the preceding part of this series, the interplanar angle in *o,o'*-dimethylbiphenyl was estimated to be about 70°, and this compound was inferred to have the *cis*-configuration. This value of the interplanar angle is considerably larger than that for dihydrodibenzoxepin, 50°, estimated by Beaven et al., or 44.5°, by the present author. Therefore, even when the value, 50° or 44.5°, is adopted as the interplanar angle in dihydrodibenzoxepin, the introduction of the substituents into the ortho positions can evidently increase the interplanar angle, and hence a decrease in the intensity and the hypsochromic shift caused by the introduction of two *o*-methyl groups can be explained sufficiently, contrary to the opinion of Braude and others. A decrease in the intensity of the band caused by the introduction of two *o*-methoxyl groups may be similarly explained by steric effect, but the fact that the band of *o,o'*-dimethoxy-derivative is at, though slightly, longer wavelengths than that of the parent compound may be attributed to the electronic effect of the substituents.

Finally, in connection with the spatial configuration of the *o,o'*-bridged biphenyls, it is noteworthy that recently Iffland and Siegel[7] succeeded first in preparing an optically active biphenyl derivative whose optical activity is due to non-planarity of the biphenyl skeleton as a consequence of the requirement of a three-carbon-atom-bridge across the *o,o'*-positions. According to them, this compound, *d*-6,6-dicarbethoxydibenzo-[a,c] [1,3]-cycloheptadiene (entry 6, Table I), is optically stable in the crystalline state, and loses half of its activity ($[\alpha]_D^{32.5}$ +2.25° in cyclohexane) in 80 min. in cyclohexane solution.

Summary

The ultraviolet absorption spectra of some *o,o'*-bridged biphenyls and their relations to the spatial configurations have been discussed. The method developed in the earlier parts of this series has been applied to these compounds, especially *o,o'*-three-atom-bridged (*o,o'*-7-membered-ring-bridged) and *o,o'*-four-atom-bridged (*o,o'*-8-membered-ring-bridged) biphenyls, and the interplanar angles have been calculated to be about 44.5~47.3° (average, 46°) for the former compounds and about 58.0~61.5° (average, 59.8°) for the latter.

The author thanks Professor Kengo Shiomi for reading the manuscript and for valuable advice.

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The Relation between the Deformation of Substrate of PVA Sheet by Stretching and the Stretch Ratio R_s

By Yoshié TANIZAKI, Teruaki KOBAYASHI and Noboru ANDO

(Received June 24, 1959)

In the hope of analyzing relative directions of transition moments of dyes by their dichroism in stretched polyvinyl alcohol (PVA) sheets, the following equation has been derived previously in reference to the relation between the observed optical density ratio R_d and the stretch ratio R_s[1],

$$R_d = \frac{2+2(2r^2-1)\,T(R_s)}{(2r^2+1)-(2r^2-1)\,T(R_s)} \tag{1}$$

where

$$\left.\begin{aligned} T(R_s) &= \frac{R_s^2}{R_s^2-1} \\ &\times\left\{1-\frac{N(R_s)}{\sqrt{R_s^2-1}}\ln(R_s+\sqrt{R_s^2+1})\right\} \\ N(R_s) &= 2 \\ &\times\left\{\frac{1}{\sqrt{R_s^2-1}}\ln(R_s+\sqrt{R_s^2-1})+R_s\right\}^{-1} \\ R_s &> 1 \end{aligned}\right\} \tag{2}$$

and the angle between the orientation axis of a molecule and the direction of its transition moment is given by $\cot^{-1}r$. When Eq. 1 was derived, it was assumed that an imaginary sphere in substrate of PVA sheet changes into a spheroid, keeping its volume constant, with the stretching of the PVA sheet. The relation between R_d and R_s expressed by Eq. 1, which was derived on the basis of such an assumption, coincided well with the experimental results of the dyes which the authors used. However, it has become necessary to ascertain whether the assumption is practically correct or not. This inspection was carried out by a very simple check measurement. Therefore, the method and the results obtained will be reported.

The object of this paper is to confirm the following subjects: 1) whether the width and the thickness of a PVA sheet decrease in the same ratio, when the sheet is stretched; 2) whether the relation between two quantities used when R_s was defined—namely the lengths of both long and short axes of an ellipse deformed from a circle drawn on the sheet by stretching it—coincides with the theoretical relation derived by assuming an ellipsoid of constant volume as just mentioned; 3) and whether if the two facts are just as expected, the relation between R_d and R_s of poly-iodine ions in PVA sheet[2], which seem to have both their transition moment and orientation axis in the same direction, must have the same behavior both experimentally and theoretically.

The Change in Width and Thickness of PVA Sheet When It Is Stretched.—The width and the thickness of PVA sheet were measured with a caliper and a micrometer. Let w_0 be the initial length of PVA sheet perpendicular to the stretching direction (the width), t_0 be the initial thickness, and w and t be their respective values corresponding to any R_s. Values of $(w/w_0)/(t/t_0)$ are plotted in Fig. 1, in which the white circles mean values when the ratio of the initial lengths of sheet parallel and perpendicular to the stretching direction is about 1 : 1, and the black circles those corresponding to the ratio of about 1 : 3. The figure shows clearly that the width and the thickness decrease in the same ratio at least in the former case (which has the same condition as the others which the authors have reported).

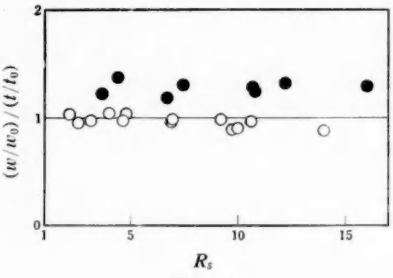

Fig. 1

1) Y. Tanizaki, This Bulletin, **32**, 75 (1959).

2) Y. Tanizaki, T. Kobayashi and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 445 (1959).

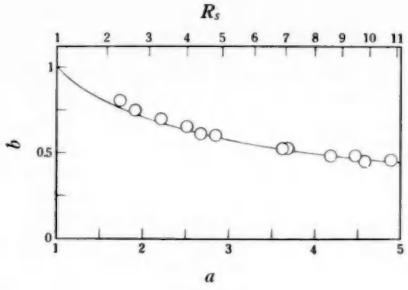

Fig. 2

The Relation between Lengths of Long and Short Axes. — Let a be the length of the long axis and b that of the short one of an ellipsoid, and then its volume is proportional to ab^2 and R_s is defined by a/b, with $a=b$ before stretching. Now, taking up a case in which the width decreases in proportion to the thickness as shown in Fig. 1, the authors searched for the following relation, to see whether the values of R_s actually used were correct. If an assumed sphere in a PVA sheet changes into ellipsoids, keeping its volume constant, when it is stretched, then the theoretical relation of $b-a$ or $b-R_s$ will be expressed by the curve shown in Fig. 2. Observed values corresponding to the curve are also shown in the figure, and they fit it satisfactorily.

The Relation between R_d and R_s of Poly-iodine Ions in PVA Sheet. — The absorption at about 600 mμ of iodine in PVA is due to linear poly-iodine ions constituted by many iodine atoms[3]. Therefore, in such a polyatomic molecule, its orientation axis coincides with the direction of its transition moment, and then the value of r mentioned above becomes infinity and Eq. 1 has the simple form of

$$R_d = [2T(R_s)] / [1-T(R_s)] \qquad (3)$$

In Fig. 3 a curve drawn by Eq. 3 is shown, and corresponding observed values are also shown by white circles. This experiment was performed as follows.

Iodine was adsorbed by PVA sheets in solutions containing boric acid ~5 g.%, potassium iodide 1~2 g.%, ammonium iodide 1~2 g.% and iodine 0.2~0.5 g.%. The sheets, which were swollen beforehand in water, were dehydrated in alcohol to be put back in a hard state, in order to

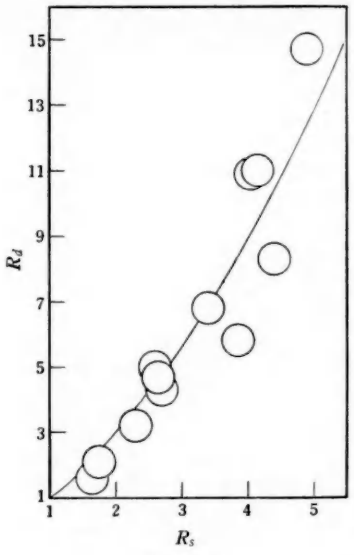

Fig. 3

prevent adsorbed iodine from fleeing from the sheets. However, even by this method, iodine could not be adsorbed in a satisfactorily uniform manner. The PVA sheets which adsorbed iodine were stretched after they were dried well at room temperature. The absorption spectra by polarized light of any stretched iodine-PVA sheet did not always show the same values at corresponding angles, when the sample sheet was rotated (0° to 360°); that is, $D_{\parallel}$ (or $D_{\perp}$) of a sample was measured at two angles, but the two observed values did not always coincide with each other. Therefore, it is their average values that are shown in Fig. 3.

The agreement between the curve drawn by Eq. 3 and the observed values is a direct verification of the propriety of distribution function which was used when Eq. 1 was derived. Therefore, if only samples which are sufficiently long as compared with their width are used, when PVA sheets are stretched, it may be considered that the deformation of their substrate occurs with a constant volume (at least when $R_s<15$). This shows that the fundamental assumption employed for the derivation of the equation was proper.

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3) See Ref. 2 and those cited in it.

Effect of Dry Grinding on Gibbsite

By Goro YAMAGUCHI and Kenichi SAKAMOTO

(Received May 26, 1959)

The crystal structure of gibbsite, one of the aluminum-trihydroxides, is a double-layered structure, and the binding force between layers is a rather weak hydrogen bond. So, when gibbsite is ground, it is supposed that the dimension of crystal particles is reduced and the stacking disorder of layers may occur. The authors examined the structural change of ground gibbsite, and confirmed the fact that very fine gibbsite (diameter of the particles is less than 1 micron) decomposes to χ-alumina directly, and in this process boehmite is not produced. The authors also studied the thermal decomposition of ground gibbsite and checked the difference of thermal properties between unground and ground gibbsite.

Experimental

Material. — Gibbsite employed in this study is a commercial product. It consists of aggregates of small crystals of a few microns and the dimension of the aggregates is 20~30 microns. Impurities are shown in Table I.

TABLE I. IMPURITIES IN GIBBSITE

Na_2O	0.35 %
Fe_2O_3	0.009
SiO_2	0.008

Procedure. — This gibbsite was ground in a ball mill and sampled. The samples were examined by X-ray methods, including X-ray small-angle diffraction procedure, and also by differential thermal analysis (DTA). Also their ignition loss was determined.

Results

Gibbsite was ground for 100 hr., and sampled at a definite time during grinding. The ignition loss was nearly constant through this process (Table II). The result of X-ray analysis was shown in Fig. 1. It is seen from this result that

TABLE II. IGNITION LOSS OF GROUND GIBBSITE

Time of grinding	Igniton loss
0 hr.	34.4 %
1	34.4
3	34.7
6	33.9
10	34.1
20	33.7
40	34.2
100	35.0

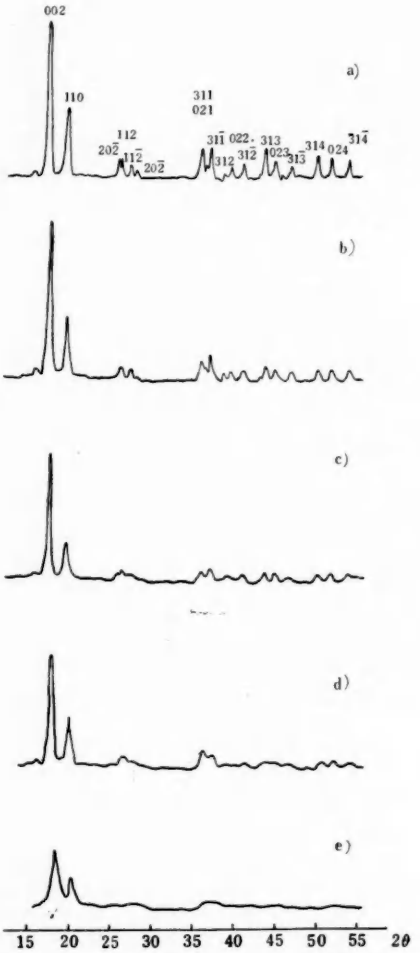

Fig. 1. X-ray diffraction diagrams of gibbsite.
a) Original gibbsite
b) Ground for 6 hr.
c) Ground for 10 hr.
d) Ground for 20 hr.
e) Ground for 100 hr.

the intensities of diffracted lines decreased gradually, and only two lines (002) and (110) were observed after 40 hr. On the contrary, the result of the small-angle scattering suffered little change (Fig. 2). From this, the authors can calculate the diameter of gibbsite by using Warren's formula[1]. Diameters of unground gibbsite and of that ground for 100 hr. are about 3500 and 2000 Å respectively. The diameter of gibbsite, ground less than 100 hr., lies between 3500 and 2000 Å. Microscopic observation reveals that an aggregate was released into some single particles, and a single particle was broken to a few fragments which have the size of about a micron. From above facts, it may be said that a particle of gibbsite which seems to be a single crystal is not continuous in the sense of X-ray crystallography. This continuous domain which is sensible for small-angle diffraction remained almost unchanged during grinding. The result of DTA was shown in Fig. 3. When the grinding time is within a few hours, ground gibbsite decomposes similarly as unground gibbsite does, that is, it reveals three endothermic peaks. But after a longer period of grinding, the DTA-curve of gibbsite changes gradually from the normal curve. The first peak becomes smaller and

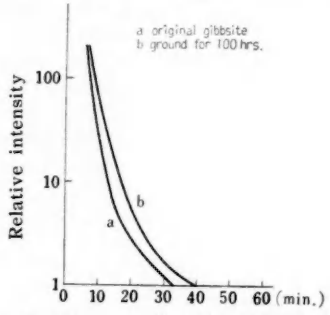

Fig. 2. X-ray small angle diffraction of gibbisite.

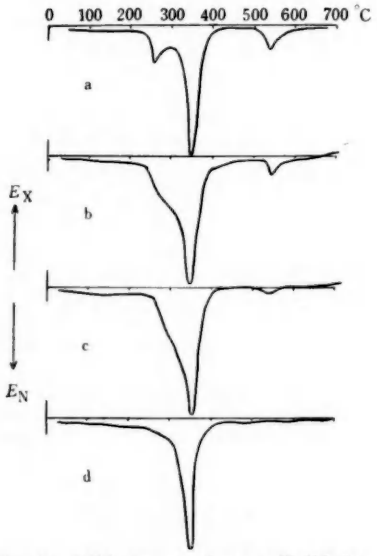

Fig. 3. DTA-curves of ground gibbsite.
a) Original gibbsite
b) Ground 6 hr.
c) Ground 20 hr.
d) Ground 40 hr.

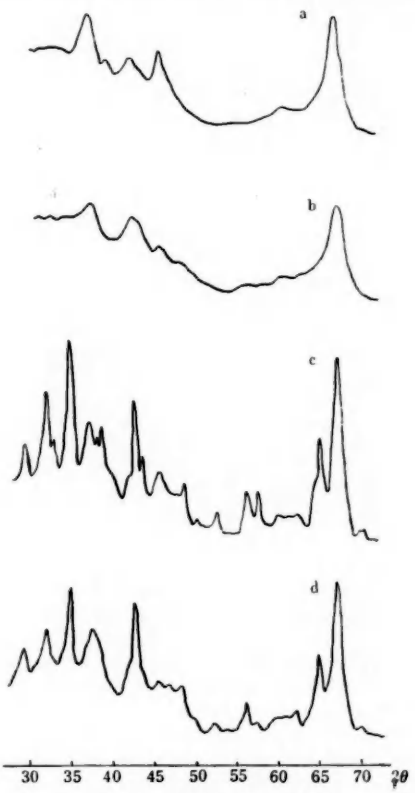

Fig. 4. X-ray diffraction diagrams of calcined gibbsite.
a) Calcined at 800°C after 3 hour-grinding [(χ+γ) alumina]
b) Calcined at 800°C after 20 hour-grinding (χ-alumina)
c) Calcined at 1000°C after 3 hour-grinding [(κ+θ) alumina]
d) Calcined at 1000°C after 20 hour-grinding (κ-alumina)

1) B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

only a knob is seen at this point. Parallel with this, the third peak becomes smaller. After the grinding of 40 hr., only the main peak is observed. This leads us to the conclusion that ground gibbsite decomposes directly into alumina; diffracted lines of alumina at 700~900°C were different from each other according to their grinding times. The diffraction of 1.99 Å became weaker and the diffraction of 2.12 Å became relatively intense (Fig. 4).

Consideration

There are many minerals, such as clay minerals, which have layered structures. In these substances the binding force within the layer is covalent and very rigid, but the interlayer force is rather weak. Lately it has been reported that there are many disordered clay minerals and theoretical calculation has been made by many authors[2].

Gibbsite, which has a composition of aluminum-trihydroxide and does not contain silicon oxide, may be said to be one of the most simple layered minerals. Therefore, it is possible to anticipate the fact that the various types of stacking along *c*-axis will occur in aluminum-trihydroxide. Thus it can also be anticipated that gibbsite, one of aluminum-trihydroxide-polytypes, is naturally supposed to be easily disordered by grinding. In this study, the authors can indicate that the properties of ground gibbsite are as follows: 1) gibbsite retains its composition during grinding; 2) the X-ray small-angle diffraction behavior suffers little change by grinding and appears within a very narrow range; 3) the intensities of diffracted lines become weak gradually with grinding; 4) (002) reflection does not diminish at first but becomes weak after a grinding of about 10 hr.; 5) (110) reflection still exists with (002) reflection after the disappearence of other lines.

From the facts mentioned above, it is clear that the disintegration of crystal occurred by grinding and the intensity of diffracted lines became weak. It may be said that only a slipping of layers took place so long as (002) reflection did not change, and after that the order along *c*-axis began to be lost with the diminution of (002) intensity. But the fact that (110) reflection remained as well as (002) after the other reflections had vanished indicates the direction of the slipping of the layers. The crystal structure of gibbsite is shown in Fig. 5 and Table III[3]. As explained already the packing of (OH) is an unusual packing of 1—2 2—1, so the direction of the slipping of layers would be [110]. In fact, it is proved that $F(110)$ is unchanged so long as the slipping of layers proceeds in the direction [110].

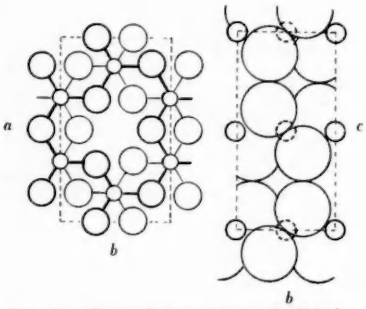

Fig. 5. Crystal structure of gibbsite.

TABLE III. CRYSTAL STRUCTURE OF GIBBSITE

Crystal class	Monoclinic
Space group	$P\,2_1/n$ (C_{2h}^5)
Unit cell	$a=8.6236$ Å, $b=5.0602$ Å
	$c=9.699$ Å, $\beta=85°26'$
Z	8 $Al(OH)_3$
Atomic coordinates	$4(e)$; $\pm(X,Y,Z;\ 1/2-X,$ $Y+1/2,\ 1/2-Z)$

As seen from Fig. 5, there are two layers with a distance of $c/2$ in a unit cell and the structure within the layer is unchanged. Thus F is separated to parts F_1 and F_2, each of which is an F-factor of its own layer. Also it is assumed that a lower layer keeps its position and an upper layer slips by $\Delta r(\Delta X+\Delta Y)$. So the displacement of any atom of an upper layer is equal to Δr. Thus

$$\begin{aligned}F(110)_{\text{slipped}} &= F_1(110)+F_2(110)\\ &= \Sigma\, 2f\cdot\cos 2\pi(X+Y)\\ &\quad +\Sigma\, 2f\cdot\cos 2\pi[(1/2-X-\Delta X)\\ &\quad +(1/2+Y+\Delta Y)]\\ &= \Sigma\, 2f\cdot\cos 2\pi(X+Y)\\ &\quad +\Sigma\, 2f\cdot\cos 2\pi[(Y-X)\\ &\quad +(\Delta Y-\Delta X)]\end{aligned}$$

2) G. W. Brindley, "X-ray Identification and Crystal Structures of Clay Minerals", Mineralogical Society, London (1951); S. B. Hendricks and E. Teller, *J. Chem. Phys.*, **10**, 147 (1942); W. H. Zachariasen, *Phys. Rev.*, **71**, 715 (1947); C. R. Houska and B. F. Warren, *J. Appl. Phys.*, **25**, 1503 (1954).

3) H. D. Megaw, *Z. Krist.*, **A87**, 185 (1934).

$$= \Sigma 2f \cdot \cos 2\pi(X+Y) + \Sigma 2f \cdot \cos 2\pi(Y-X) \quad (\Delta X = \Delta Y) = F(110)_{\text{original}}$$

In a disordered structure, the magnitude of the slipping is not constant but it is natural that (OH) of disordered gibbsite has nearly hexagonal close stacking in short range.

Many reports about the thermal decomposition of gibbsite have been published[4]. Brown and coworkers proposed the dual decomposition hypothesis of gibbsite as follows[5].

$$\begin{array}{l} \text{Gibbsite} \rightarrow \chi \rightarrow \kappa \rightarrow \alpha \\ \quad\downarrow \qquad\qquad\qquad\uparrow \\ \text{Boehmite} \rightarrow \gamma \rightarrow \delta \rightarrow \theta \end{array}$$

Also Tertian and coworker showed that very fine gibbsite decomposed directly to χ-alumina without being contaminated with boehmite[6].

$$\text{Gibbsite} \rightarrow \chi \rightarrow \kappa \rightarrow \alpha$$

When the authors were writing this report, Dr. Tertian sent us kindly very fine gibbsite which had the diameter of about 0.5 micron. So the thermal transformation of this gibbsite was checked and, consequently, it could be recognize that Tertian's result was correct. (Fig. 6)

In reference to the above facts, it is expected that after long grinding, it is possible to get fine gibbsite which does not decompose into boehmite but is transformed directly into χ-alumina. The result of DTA shows that the first peak and the third peak which indicate respectively formation and decomposition of boehmite become smaller with the duration of grinding. Parallel to this, the dimension of ground crystal decreased to a micron. After 40 hr. grinding, gibbsite decomposed to alumina which did not contain boehmite. This alumina exhibited the characteristic diffraction of 2.12 Å for χ-alumina and was transformed to κ-alumina. So it may be concluded that the ground gibbsite has the same properties as the fine gibbsite. But there are some questions in this explanation. This ground gibbsite shows only two diffraction lines and is no longer true gibbsite. But it may be supposed that this

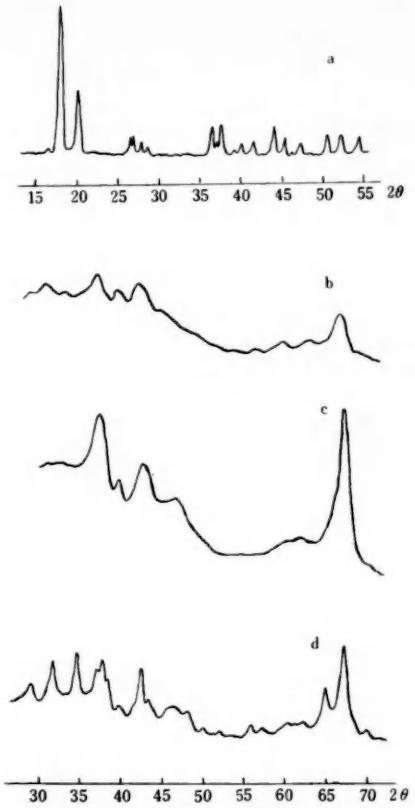

Fig. 6. X-ray diffraction diagrams of fine gibbsite.
a) Original gibbsite
b) Calcined at 350°C
c) Calcined at 800°C (χ-alumina)
d) Calcined at 1000°C (κ-alumina)

gibbsite retains the essential property and structure after being ground, so the thermal property of this gibbsite would have the true character of gibbsite.

The difference of thermal property between large and small particles of gibbsite is explained as follows. When large particles of gibbsite is heated to about 200°C, the hydrothermal reaction begins to form interior crystals and dissolution of gibbsite and crystallization of boehmite occur[7]. But in the case of fine particles, the small crystal can not keep the vapor pressure in it, and the vapor evaporates, so the formation of boehmite ceases. Then the gibbsite decomposes to χ-alumina. That is, the formation

4) A. S. Russell et al., "Alumina Properties, Technical Paper No. 10", Aluminum Company of America, Pittsburgh, Penn. (1956).
5) J. F. Brown et al., *J. Chem. Soc.*, **1953**, 84.
6) R. Tertian and D. Papee, *Compt rend.*, **241**, 1575 (1955).
7) G. Yamaguchi and K. Sakamoto, This Bulletin, **32**, 696 (1959).

of boehmite is not the result of direct decomposition but the result of hydrothermic reaction as in an autoclave, while the small particles of gibbsite can not keep the vapor pressure in it. Thus the hydrothermic reaction does not occur and boehmite is not produced from this gibbsite.

Summary

The effect of dry grinding on gibbsite was examined by X-ray diffraction, X-ray small angle diffraction and differential thermal analysis. It has been found that there are two sorts of structural change in the process of dry grinding. One, which occurs early in this process, is the slip of layers. In this stage (002) reflection retains its intensity. The other, which takes place after grinding of about 10 hr., is the three-dimensional disintegration of the crystal structure and the intensities of all diffractions become weak. Since only two reflections (002) and (110) are observed after 40 hr., it can be known that the direction of the slipping of layers is [110].

DTA-curve of gibbsite exhibits three endothermic peaks in the beginning of grinding but comes to exhibit only one peak which indicates the decomposition of gibbsite to alumina. This means that ground gibbsite decomposes directly to χ-alumina as fine gibbsite and boehmite is not produced in this process.

The authors wish to express hearty thanks to Dr. R. Tertian of Pechiney for his favor.

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Sur la dissolution des minerais sulfurés en divers milieux. I. Dissolution d'un minerai sulfuré de fer en milieu acide

Par Masami ICHIKUNI et Hiroshi KAMIYA

(Reçu le 29 mai 1959)

La désagrégation des minerais sulfurés a été étudiée au point de vue de prospection géochimique par Ohashi[1], qui s'est préoccupé à la dissolution du fer, cuivre, zinc et plomb dans les conditions des eaux naturelles. Garrels en a développé une discussion se basant sur les notions thermodynamiques d'équilibre des reactions[2]. La connaissance du comportement du soufre n'est pas pourtant satisfaisante pour l'explication complète de la désagrégation. D'ailleurs l'influence des facteurs de milieu sur ce phénomène reste encore peu claire. L'examen détaillé du phénomène, par voie de cinétique de la réaction, serait d'une importance particulière dans la géochimie.

On pourrait désigner le pH, le potentiel d'oxydo-réduction, la température, la concentration en ion sulfate et d'autres comme facteurs de milieu participant à la désagrégation. Dans ce rapport on présentera une étude fondamentale sur l'influence du pH et de l'air, celui-ci se rapportant avec le pH au potentiel d'oxydoréduction.

1) S. Ohashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 845, 901 (1953).
2) R. M. Garrels, *Geochim. et Cosmochim. Acta*, **5**, 153 (1954).

Expérience

Généralité. — On pulvérise du minerai sulfuré de fer frais, en traite en milieu acide ou neutre en conduisant de l'air dans la suspension du minerai et poursuit la concentration de composants dissous en fonction du temps.

Echantillon.—Un minerai siliceux (nom populaire donné à un minerai sulfuré consistant en

TABLEAU I. RÉSULTAT D'ANALYSE DU MINERAI

Composant	Teneur, %
SiO_2	71,0
Fe	13,3
S combiné	15,0
S libre	0,15
Cu	0,048
Total	99,5

sulfure de fer et en acide silicique qui se produit autour d'un filon de minerai sulfuré chalcophile) produit à la mine de Kosaka, département d'Akita. On l'a pulvérisé de manière à ce que la poudre passe par un tamis avec un nombre de maille à 100. Le tableau I en montre le résultat d'analyse et révèle que le minerai consiste presque entièrement en pyrite et en acide silicique.

La présence du soufre libre dans le minerai pulvérisé suggère la décomposition du minerai provoquée par l'oxydation lors de la pulvérisation. Il y a donc une possibilité d'altération partielle du minerai sulfuré en d'autres composés que le sulfure, tels que l'oxyde, le sulfate.

Traitement. — On prend 200 ml. d'acide chlorhydrique à une concentration connue ou d'eau bidistillée dans un ballon à fond plat à 300 ml. et le met sur un bain-marie. On en attache à l'entrée un tuyau de verre qui a 4 mm. de diamètre et qui sert à introduire de l'air dans la liqueur et un condensateur à reflux dont la sortie est reliée à une trompe, réglée de manière à ce que l'air barbote dans la liqueur à un débit constant. La température de la liqueur est réglée à 80°C. On y ajoute 5 g. de minerai pulvérisé et effectue le prélèvement d'une petite quantité de liqueur, à peu près 10 ml., à 10 min., une, deux, trois et quatre heures à partir du moment de l'addition du minerai. Le dosage du cuivre, fer et sulfate s'effectue sur la liqueur filtrée.

Conditions du traitement.—Les facteurs à examiner sont le débit de l'air et le pH. Etant donné que la désagrégation des minerais sulfurés donne de l'acide sulfurique, les essais de la dissolution en milieu acide sulfurique se conformeraient aux conditions dans la nature. Mais le dosage du sulfate formé par le traitement rencontrera une difficulté, l'augmentation de la concentration en sulfate devant être très légère. Par suite de cette considération, on s'est permis d'employer l'acide chlorhydrique. On maintient la température constamment à 80°C sur toute la série des expériences, afin de supprimer l'effet de la température lors de la comparaison des résultats.

TABLEAU II. CONDITIONS DU TRAITEMENT ET CONCENTRATION DE COMPOSANT DISSOUS

Conditions		Durée du traitement	Concn. des composants dissous				
Concn. en HCl N	Débit de l'air l./min.		Cu^{2+}	Fe^{2+}	Fe^{3+}	SO_4^{2-}	acidité
		hr.			mé/l.		
		1/6	0,039	1,69	0,06	1,50	
		1	0,070	1,85	0,01	1,50	
0,1	0	2	0,090	1,86	0,04	1,56	
		3	0,099	1,87	0,03	1,56	
		4	0,114	1,93	0,09	1,63	
		1/6	0,031	1,43	0,10	1,25	
		1	0,041	1,72	0,00	1,37	
0,1	0,5	2	0,062	1,74	0,06	1,50	
		3	0,091	1,75	0,05	1,50	
		4	0,108	1,87	0,00	1,54	
		1/6	0,031	1,61	0,03	1,25	
		1	0,049	1,95	0,03	1,58	
0,1	1,5	2	0,077	2,10	0,04	—	
		3	0,083	2,25	0,14	2,08	
		4	0,100	2,48	0,02	2,13	
		1/6	0,013	1,58	0,00	1,21	
		1	0,024	1,93	0,00	1,46	
0,01	1,5	2	0,049	2,12	0,00	1,73	
		3	0,062	2,35	0,00	1,88	
		4	0,079	2,56	0,04	2,19	
		1/6	0,007	1,36	0,01	1,35	
		1	0,012	1,68	0,01	1,46	
0,001	1,5	2	0,020	1,82	0,00	1,83	
		3	0,028	2,12	0,02	2,08	
		4	0,032	2,39	0,00	2,50	0,11
		1/6	0,002	1,15	0,03	1,46	0,31
		1	0,002	1,31	0,00	1,67	0,36
Eau bidistillée	1,5	2	0,003	1,36	0,00	1,81	0,45
		3	0,008	1,43	0,00	2,19	0,76
		4	0,012	1,49	0,02	2,71	1,22

Les essais du débit de l'air s'effectuent en milieu acide chlorhydrique 0,1 N. Le débit de l'air est varié d'une façon suivante: 1) sans introduction de l'air, 2) 0,5 l./min., et 3) 1,5 l./min. Le premier essai ne signifie pas l'exclusion entière de l'air, mais la diminution la plus possible de contact avec l'air. On a recours en même temps à un agitateur mécanique dans le but de maintenir l'efficacité constante de l'agitation.

Les essais du pH s'effectuent sous un débit de l'air de 1,5 l./min., en milieu acide chlorhydrique: 1) 0,1 N, 2) 0,01 N, 3) 0,001 N, et 4) dans l'eau bidistillée.

Analyse. — Une quantité limitée de liqueur prélevée ayant empêché d'effectuer une analyse complète, on se borne à faire le dosage du cuivre, fer divalent, fer total et sulfate. Le cuivre et le fer sont dosés par la colorimétrie, avec la dithizone et l'*o*-phénanthroline, respectivement. Le sulfate, par la turbidimétrie après la formation du sulfate de baryum.

On ne décèle pas dans la liqueur d'autres composants de soufre que le sulfate.

Résultats et discussion

Le tableau II montre le résultat obtenu. Lors du traitement avec de l'eau bidistillée ou de l'acide très dilué, on a remarqué la formation de l'acide sulfurique dont la quantité est estimée par la soustraction du fer du sulfate, les deux étant exprimés en mé/l. Par des essais effectués à part, on a constaté que la somme du fer et de l'acidité s'accorde bien avec la quantité de sulfate dans la limite d'erreur du dosage.

D'autre part, la teneur en fer trivalent est donnée par la différence entre le fer total et le fer divalent.

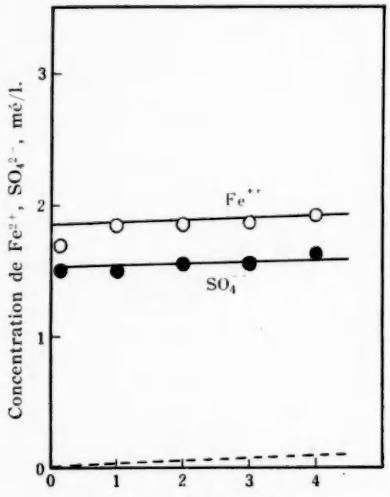
Interprétation des données. — Le minerai utilisé pour ces essais a subi une décomposition partielle par la pulvérisation, ce qui cause quelques irrégularités de dissolution au début du traitement. On développera la discussion en tenant compte de la quantité de composants dissous provenant de la partie préalablement décomposée du minerai.

Les figures sont dessinées avec les données du tableau II. La figure 1 représente la dissolution du fer et du sulfate, et la figure 2, celle du cuivre.

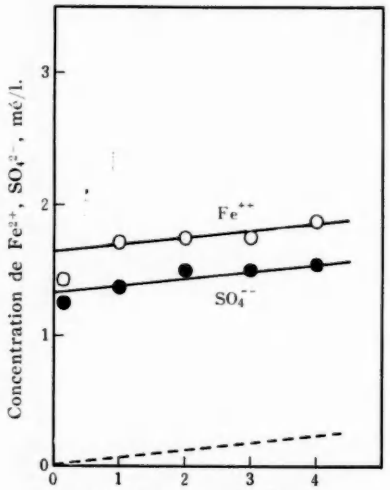
Dans les figures, le trait plein représente la concentration de composants telle qu'on l'a trouvée, et le trait discontinu, tracé de l'origine parallèlement à celui-là, en montre la concentration correspondant à la dissolution par le traitement. La pente du trait discontinu permet de comparer la vitesse de dissolution d'un composant avec celle d'autres.

Influence du débit de l'air. — Ces essais, effectués en milieu acide chlorhydrique 0,1 N, montrent que la dissolution du cuivre en subit peu d'influence, tandis que celle du fer et du soufre est favorisée par l'augmentation du débit de l'air.

Influence du pH. — La vitesse de dissolution du fer est la même dans l'acide chlorhydrique 0,1 N que dans l'acide 0,01 N. Il en est de même du cuivre et du soufre. L'élévation du pH empêche la dissolution du cuivre et du fer, et accélère celle du soufre.



(a) HCl 0,1 N; Air 0 l./min.



(b) HCl 0,1 N; Air 0,5 l./min.

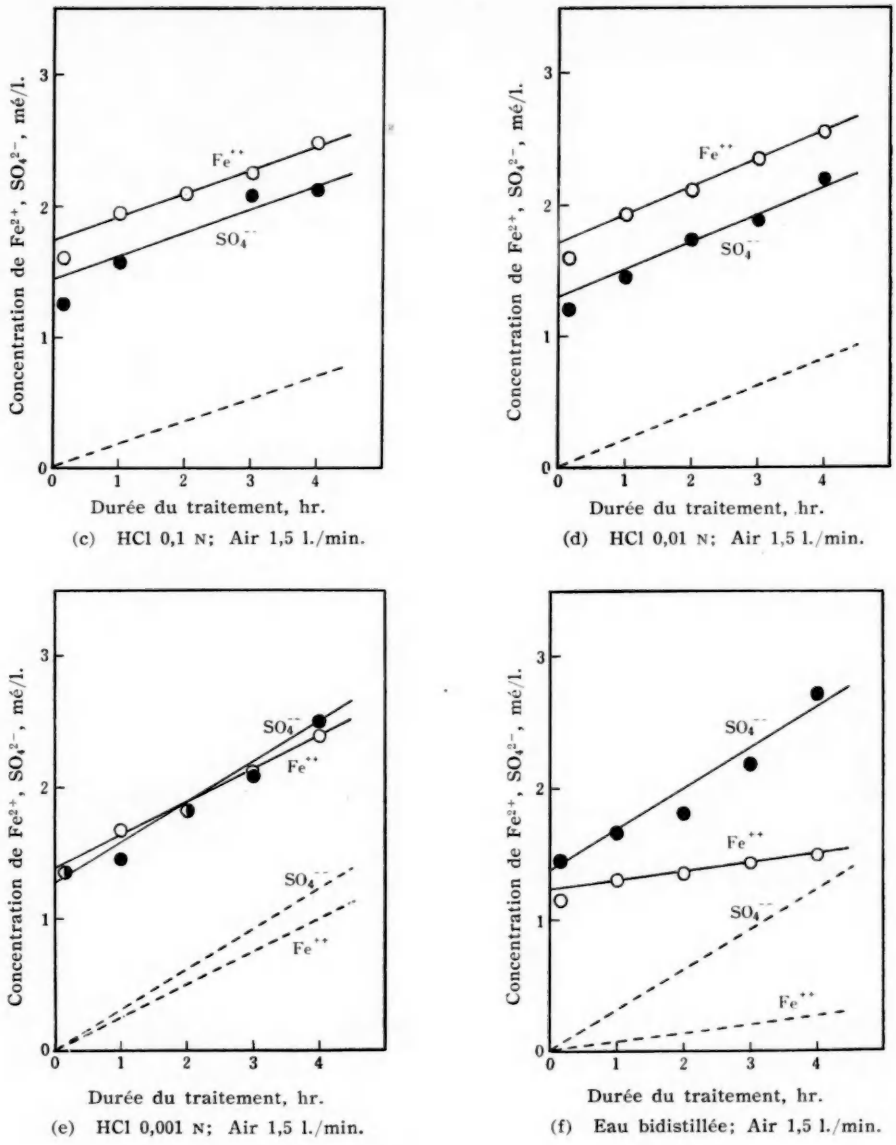

Concentration de Fe^{2+}, SO_4^{2-}, mé/l.
Fe^{++}
SO_4^{--}
Durée du traitement, hr.
(c) HCl 0,1 N; Air 1,5 l./min.
(d) HCl 0,01 N; Air 1,5 l./min.
(e) HCl 0,001 N; Air 1,5 l./min.
(f) Eau bidistillée; Air 1,5 l./min.

Fig. 1. Dissolution du fer et du sulfate.
Trait plein: concentration totale.
Trait discontinu: concentration correspondant à la dissolution par le traitement.

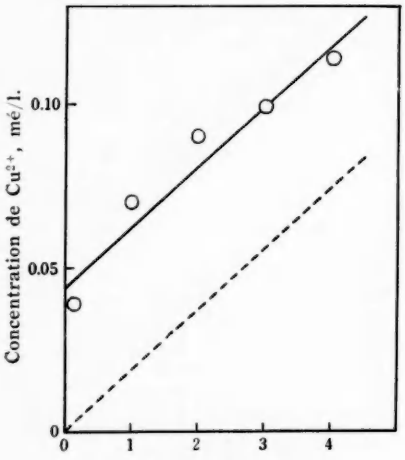
Aucune variation de pH n'a été trouvée pour les expériences effectuées en milieu acide 0,1 N et 0,01 N. Cependant on a remarqué l'abaissement du pH au cours du traitement dans l'acide 0,001 N et l'eau bidistillée. Dans le premier cas, le pH de la liqueur était de 3,0 avant l'addition du minerai, et de 2,8 après quatre heures du traitement. On discutera plus loin le dernier cas, dissolution du minerai par l'eau.

Composition de composants dissous. — La quantité de cuivre dissous étant très petite par rapport à celle de fer et de sulfate,

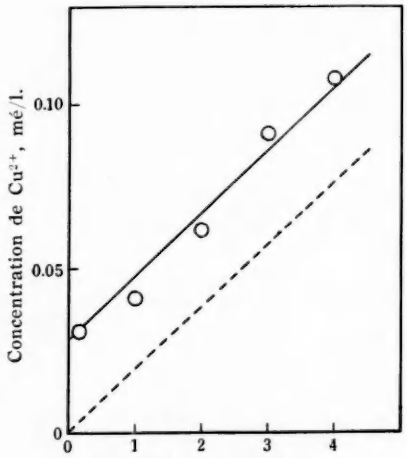
on étudie ici simplement la relation entre le fer et le sulfate. La concentration de fer trivalent ne dépassant pas quelques pourcents de celle de fer divalent, on ne prend pas non plus celui-là en considération. Comme l'indique la figure 1, le rapport de la quantité de fer divalent sur celle de sulfate est l'unité, tous deux étant produits par le traitement et exprimés en unité de mé. On voit bien que l'oxydation du minerai sulfuré par l'air donne le sulfate de fer(II). La présence du fer trivalent serait attribuable à l'oxydation du fer divalent sous forme duquel le fer contenu dans le minerai se dissout dans l'eau.

Si la réaction a lieu dans un milieu à pH relativement grand, le sulfate se dissout plus que le fer. Cela s'explique par la formation de l'acide sulfurique. Ce phénomène devient plus remarquable lors du traitement avec de l'eau bidistillée.

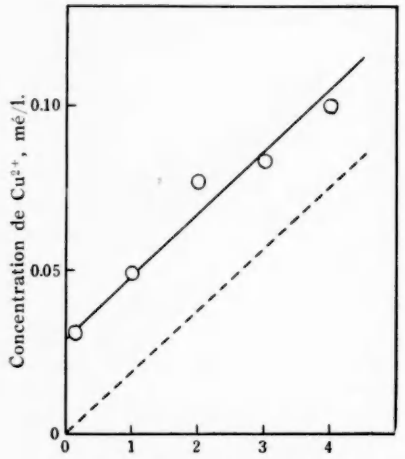
Dissolution du minerai par l'eau.—Le résultat de cet essai, considéré comme reproduction de la désagrégation du minerai sulfuré par les eaux naturelles de caractère normal, serait indispensable pour la connaissance des réactions qui ont lieu dans la nature. La dissolution du fer devient



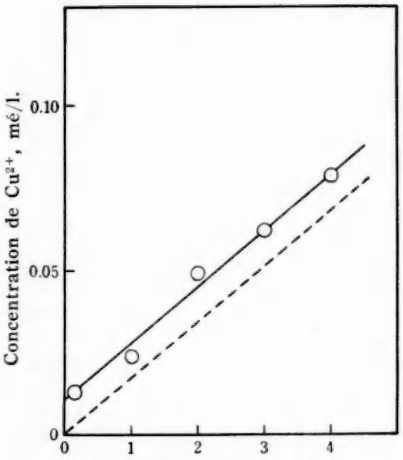
(a) HCl 0,1 N; Air 0 l./min.



(b) HCl 0,1 N; Air 0,5 l./min.



(c) HCl 0,1 N; Air 1,5 l./min.



(d) HCl 0,01 N; Air 1,5 l./min.

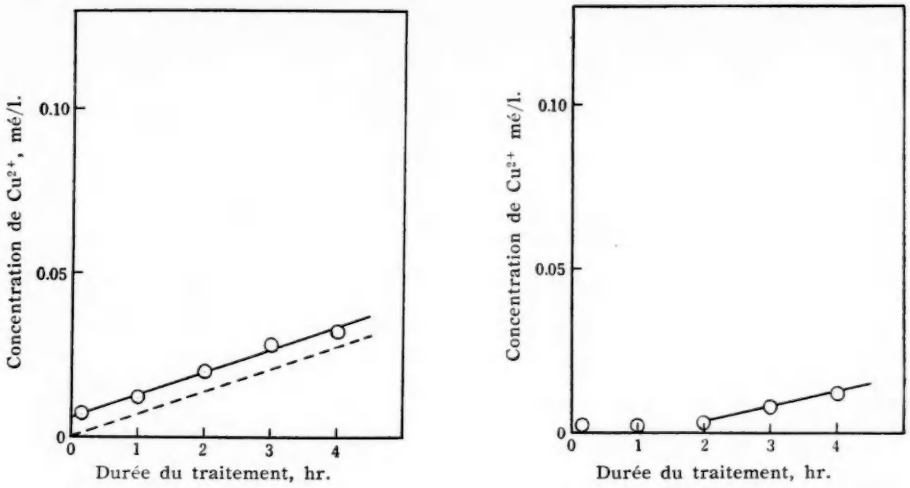


Fig. 2. Dissolution du cuivre
Trait plein: concentration totale.
Trait discontinu: concentration correspondant à la dissolution par le traitement.

extrêmement petite, et on ne décèle presque pas de cuivre. Celle du sulfate, au contraire, s'accélère dans ce milieu.

Pourtant on n'arrive pas à différer si une faible concentration en fer est causée par la précipitation du fer hydrolysé ou par la prédominance de la réaction de formation de l'acide sulfurique.

La liqueur devient acide avec la durée du traitement, et au bout de quatre heures, le pH en est inférieur à 3. La dissolution du cuivre augmente avec l'abaissement du pH. Cette tendance est prévue par des essais décrits ci-dessus.

Comportements des composants.—*Cuivre.*—Le facteur règnant sur la dissolution du cuivre contenu dans le minerai sulfuré est vraisemblablement le pH du milieu. Dans un milieu à pH inférieur à 2, la vitesse de dissolution reste constante, indépendamment du pH. Elle est peu influencée par le débit de l'air introduit dans la liqueur.

Fer.—Le débit de l'air exerce une influence considérable sur la dissolution de ce métal. Le résultat des essais fait présumer que la pyrite est relativement stable, même en milieu acide, s'il s'agit des conditions non-oxydantes.

Soufre.—Cet élément se dissout sous forme de sulfate, en milieu acide ou neutre, et en présence de l'air. Sous ces conditions oxydantes, le sulfate est toujours le plus stable parmi les espèces de composés de soufre[3]. La vitesse de dissolution en est d'autant plus grande que le pH est grand, mais le mécanisme de la formation de l'acide sulfurique restera comme un problème à résoudre. Le comportement du soufre résiduel après la dissolution du sulfate de fer, $FeSO_4$, à partir de la pyrite, FeS_2, exigera une étude plus approfondie.

Les auteurs expriment leurs remerciements profonds à Monsieur le professeur K. Noguchi qui leur a permis l'exécution de cette étude et qui leur a accordé toutes les aides possibles, et à Monsieur le professeur T. Hanya qui a bien voulu leur donner des conseils utiles.

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The Infrared Spectrum of Dimethyl Sulfone

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In the preceding paper[1] normal vibrations and force constants of the methanesulfonate ion were determined empirically. In this paper the infrared spectrum of dimethyl sulfone was measured, the normal vibrations of this molecule were calculated using force constants of the methanesulfonate ion, and they were compared with the experimental values.

Calculation of Normal Vibrations

The calculation was done by means of Wilson's method[2] and treated as a five-body problem assuming the methyl radical to be one particle. As the intramolecular potential, Urey-Bradley field[3] was assumed as done in the case of the methanesulfonate ion[1]. By assuming all the valence angles of sulfur to be tetrahedral, the following clements of G and F materices were obtained[4].

Elements of G matrix for A_1 type vibrations

$$g_{11}=\frac{2}{3}\mu_S+\mu_{Me}$$

$$g_{12}=-\frac{2}{3}\mu_S$$

$$g_{13}=\frac{2}{\sqrt{3}}(\sigma'-1)\mu_S$$

$$g_{14}=-\frac{\sqrt{8}}{3}(\sigma'+1)\mu_S$$

$$g_{22}=\frac{2}{3}\mu_S+\mu_O$$

$$g_{23}=-\frac{2}{\sqrt{3}}(\sigma'-1)\mu_S$$

$$g_{24}=\frac{\sqrt{8}}{3}(\sigma'+1)\mu_S$$

$$g_{33}=\frac{3}{2}(\sigma'^2\mu_{Me}+\mu_O)+2(\sigma'-1)^2\mu_S$$

$$g_{34}=-\frac{1}{\sqrt{6}}\{3(\sigma'^2\mu_{Me}-\mu_O)+4\sigma'(\sigma'-1)\mu_S\}$$

$$g_{44}=\sigma'^2\mu_{Me}+\mu_O+\frac{4}{3}(\sigma'+1)^2\mu_S$$

Elements of F matrix for A_1 type vibrations

$$f_{11}=K_{SMe}+2(s^2_{Me}F_{Me}+t^2_{MeO}F'_{MeO}+s^2_{MeO}F_{MeO})$$

$$f_{12}=-2(t_{MeO}t_{OMe}F'_{MeO}+s_{MeO}s_{OMe}F_{MeO})$$

$$f_{13}=\sqrt{\frac{2}{3}}\{(t_{MeO}s_{OMe}F'_{MeO}+t_{OMe}s_{MeO}F_{MeO})+\sigma t_{Me}s_{Me}(F'_{Me}+F_{Me})\}$$

$$f_{14}=\sigma t_{Me}s_{Me}(F'_{Me}+F_{Me})$$

$$f_{22}=K_{SO}+2(t^2_{OMe}F'_{MeO}+s^2_{OMe}F_{MeO}+s^2_OF_O)$$

$$f_{23}=\sqrt{\frac{2}{3}}(t_{OMe}s_{MeO}F'_{MeO}+t_{MeO}s_{OMe}F_{MeO}-t_Os_O(F'_O+F_O)\}$$

$$f_{24}=-t_Os_O(F'_O+F_O)$$

$$f_{33}=\frac{1}{3}\{\sigma^2(H_{Me}-s^2_{Me}F'_{Me}+t^2_{Me}F_{Me})+(H_O-s^2_OF'_O+t^2_OF_O)\}$$

$$f_{34}=\frac{1}{\sqrt{6}}\{-\sigma^2(H_{Me}-s^2_{Me}F'_{Me}+t^2_{Me}F_{Me})+(H_O-s^2_OF'_O+t^2_OF_O)\}$$

$$f_{44}=\frac{1}{2}\{\sigma^2(H_{Me}-s^2_{Me}F'_{Me}+t^2_{Me}F_{Me})+(H_O-s^2_OF'_O+t^2_OF_O)\}+\frac{3}{\sqrt{8}}\kappa/r^2_{SO}$$

Elements of G and F matrices for A_2 type vibration

$$g=\frac{3}{2}\sigma'^2\mu_{Me}+\frac{3}{2}\mu_O+\frac{1}{3}(5\sigma'^2+2\sigma'+5)\mu_S$$

$$f=\sigma(H_{MeO}-s_{MeO}s_{OMe}F'_{MeO}+t_{MeO}t_{OMe}F_{MeO})-\frac{1}{\sqrt{8}}\kappa/r^2_{SO}$$

Elements of G matrix for B_1 type vibrations

$$g_{11}=\frac{4}{3}\mu_S+\mu_{Me}$$

$$g_{12}=-\frac{2}{3}(\sigma'+3)\mu_S$$

$$g_{22}=\frac{1}{2}\sigma'^2\mu_{Me}+\frac{3}{2}\mu_O+\frac{1}{3}(\sigma'+3)^2\mu_S$$

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Elements of F matrix for B_1 type vibrations

$$f_{11}=K_{SMe}+2(t^2_{MeO}F'_{Me}+t^2_{MeO}F'_{MeO}+s^2_{MeO}F_{MeO})$$

$$f_{12}=\sqrt{2}\,(t_{MeO}s_{OMe}F'_{MeO}+t_{OMe}s_{MeO}F_{MeO})$$

$$f_{22}=\sigma(H_{MeO}-s_{OMe}s_{MeO}F'_{MeO}+t_{MeO}t_{OMe}F_{MeO})+\frac{3}{\sqrt{8}}\kappa/r^2_{SO}$$

Elements of G matrix for B_2 type vibrations

$$g_{11}=\frac{4}{3}\mu_S+\mu_O$$

$$g_{12}=-\frac{2}{3}(3\sigma'+1)\mu_S$$

$$g_{22}=\frac{3}{2}\sigma'^2\mu_{Me}+\frac{1}{2}\mu_O+\frac{1}{3}(3\sigma'+1)^2\mu_S$$

Elements of F matrix for B_2 type vibrations

$$f_{11}=K_{SO}+2(t^2_{OMe}F'_{MeO}+s^2_{OMe}F_{MeO}+t^2_{O}F'_{O})$$

$$f_{12}=\sqrt{2}\,\sigma(t_{OMe}s_{MeO}F'_{MeO}+t_{MeO}s_{OMe}F_{MeO})$$

$$f_{22}=\sigma(H_{MeO}-s_{OMe}s_{MeO}F'_{MeO}+t_{MeO}t_{OMe}F_{MeO})+\frac{3}{\sqrt{8}}\kappa/r^2_{SO}$$

where, K is the stretching force constant, H is the bending force constant and F and F' are repulsive force constants. And μ is the reciprocal of the atomic weight of sulfur, oxygen or the methyl radical.

The following notations are also used:

$$s_{ij}=(r_i-r_j\cos\alpha_{ij})/q_{ij},$$

$$s_i=(r_i-r_j\cos\alpha_i)/q_{ij},\quad t_{ij}=r_j\sin\alpha_{ij}/q_{ij},$$

$$t_{ji}=r_i\sin\alpha_{ij}/q_{ij},\quad \sigma=r_{SMe}/r_{SO},\quad \sigma'=1/\sigma,$$

κ (intramolecular tension)

$$=-(K'_ir_{ij}{}^2+H'_{ij}r_{ij}q_{ij}\sqrt{t_{ij}t_{ji}}),$$

where r denotes S–O or S–Me bond length, q_{ij} denotes distance between non-bonded atoms, α_{ij} denotes valence angle and $r^2_{ij}=r_ir_j$.

For the S–O and S–Me bond length, the following values were assumed. S–O=1.43 Å, S–Me=1.80 Å[5].

Force constants were transferred from methanesulfonate ion[1], diethyl sulfide[6], tetramethyl silane[7] and sulfur dioxide[8]. Their values are given in Table I.

TABLE I. FORCE CONSTANTS

F. C.	10^5 dyn./cm.	Ref.	F. C.	10^5 dyn./cm.	Ref.
K_{SMe}	3.05	1)	F'_{Me}	−0.020	7)
K_{SO}	9.86	8)	F_O	0.64	1)
H_{Me}	0.157	6)	F'_O	−0.064	1)
H_O	0.552	1)	F_{MeO}	0.35	1)
H_{MeO}	0.250	1)	F'_{MeO}	−0.035	1)
F_{Me}	0.200	7)	κ	0.328*	1)

* Unit is 10^{-11} dyn./cm.

Results and Discussion

The calculated normal vibrations are given in Table II. The infrared spectrum of dimethyl sulfone in a solid state is shown in Fig. 1. The absorption frequencies are compared with the observed values and their assignments are made as shown in Table III.

TABLE II. CALCULATED NORMAL VIBRATIONS (in cm^{-1})

Type	Wave number	Assignment
A_1	741	S–Me stretching
	314	$S(Me)_2$ bending
	1252	S–O stretching
	521	SO_2 bending
A_2	408	twisting
B_1	795	S–Me stretching
	472	$S(Me)_2$ rocking SO_2 wagging
B_2	1345	S–O stretching
	428	$S(Me)_2$ wagging SO_2 rocking

TABLE III. ABSORPTIONS AND ASSIGNMENTS (in cm^{-1})

Wave number	Assignment	Calcd.
3024 (m), 2962 (w)	C–H stretching	
1430 (m), 1412 (m)	CH_3 degenerated bending	
1337 (s)	CH_3 symmetric bending	
1315 (s), 1290 (s)	S–O stretching	1345
1130 (s)	S–O stretching	1252
938 (s)	Me rocking	
761 (s)	S–Me stretching	795
695 (m)	S–Me stretching	741

C–H stretching frequencies have higher wave numbers than those of hydrocarbons because of strong electronegativity of $-SO_2-$ group. This phenomenon was also found in the case of lower sulfonates[9]. Methyl rocking vibration at 938 cm^{-1} has lower wave number than that of methanesulfonate ion. The reason may be attributed to the coupling with S–O stretching vibration.

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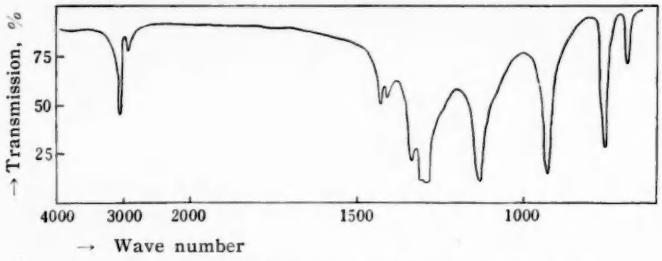

Fig. 1. Infrared spectrum of dimethyl sulfone.

The deviation between the observed and calculated frequencies may be attributed to the high value of S–O stretching force constant and the low value of O–O repulsive force constants.

Experimental

The infrared spectrum was obtained by a Perkin-Elmer Model 21 double-beam infrared spectrophotometer using NaCl prism. The KBr disk method was employed to obtain the spectrum in solid state.

Dimethyl sulfone was prepared by oxidation of dimethyl sulfoxide with hydrogen peroxide in acetic acid solution[10]. After the reaction mixture was treated with acetaldehyde and the solvent was removed, dimethyl sulfone was recrystallized from ethanol. The melting point of this compound is 108.5°C and the referenced value is 109°C[11].

The author wishes to express his indebtedness to Dr. A. Kotera, Professor of Tokyo University of Education, and Dr. T. Shimanouchi, Professor of the University of Tokyo, under whose kind direction this work was performed. The author also wishes to thank Mr. Y. Ikegami, Fellow of Tohoku University, for his co-operation in obtaining infrared spectrum, and to Mr. Y. Akai, Chief of Research Section of Funakawa Refinery, for his encouragement of this research.

Nippon Mining Co., Funakawa Refinery
Oga-shi, Akita

10) L. Fied and J. W. McFarland, *J. Am. Chem. Soc.*, 75, 5582 (1953).

11) "Beilsteins Handbuch der Organischen Chemie", E. II 1, Julius Springer, Berlin (1941), p. 277.

The Kinetics of Substitution Reactions Involving Metal Complexes. II. Effect of Acetate Ions on the Reaction between Copper(II) and Lead-Ethylenediaminetetraacetate Complexes

By Nobuyuki TANAKA and Kiyoko KATO*

(Received July 3, 1959)

In the previous paper[1], the substitution reaction of copper(II) ions and lead-ethylenediaminetetraacetate(EDTA) complexes was reported. The rate of the reaction was followed by measuring the change of the polarographic diffusion current of copper(II) ions with time in acetate buffer solutions. The reaction was found to proceed, under the experimental conditions, simultaneously through three different reaction paths, and the rate constants of the elementary reactions of those reaction paths were determined.

Although the reaction rate was measured in acetate buffer solutions, the effect of acetate ion concentration was not taken into consideration, all measurements being

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1) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, 31, 283 (1958).

carried out at 0.1 M of acetate in concentration. Ackermann and Schwarzenbach[2] found that the overall reaction rate of the substitution reaction of copper(II) ions and cadmium-EDTA complexes increased with the decreasing concentration of acetate ions, but they gave no quantitative explanation of this phenomenon. The increase of the reaction rate with the decrease of the acetate ion concentration was also found by the present authors in the case of the substitution reaction of copper(II) ions and lead-EDTA complexes.

In this paper, the effect of acetate ions on the rate of the substitution reaction of copper(II) ions and lead-EDTA complexes is investigated. The experimental results reported in the previous paper[1] are treated on the basis of the formation of acetato complexes of metal ions in acetate media and on the assumption that the substitution reaction proceeds through the hydrated metal ions which are in equilibrium with the acetato complexes. The rate constants of the elementary reactions reported previously are recalculated with the equations newly derived.

Derivation of the Rate Equation

Let us consider the acetate buffer solution which contains copper(II) ions and lead-EDTA complexes. In the solution containing acetate ions less than 0.2 M in concentration, copper(II) and lead(II) form mono- and diacetato complexes[3]. Therefore, the overall substitution reaction is represented by the equations

$$Cu^{2+} + 2\,OAc^- \rightleftharpoons CuOAc^+ + OAc^- \rightleftharpoons Cu(OAc)_2 \quad (1)$$

$$Cu^{2+} + PbY^{2-} \rightleftharpoons CuY^{2-} + Pb^{2+} \quad (2)$$

$$Pb^{2+} + 2\,OAc^- \rightleftharpoons PbOAc^+ + OAc^- \rightleftharpoons Pb(OAc)_2 \quad (3)$$

where Y^{4-} means a completely dissociated EDTA anion. Under the condition that lead ions and lead-EDTA complexes are present in a large excess over copper(II) ions, the substitution reaction 2 can be simplified to

$$Cu^{2+} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} CuY^{2-}$$

In the polarographic measurement in acetate media, it is impossible to determine separately either the concentration of hydrated copper(II) ions or that of acetato-copper(II) complexes. On the contrary, the diffusion current of copper(II) obtained in acetate media corresponds to the sum of the diffusion current of the hydrated copper(II) ions and that of the acetato-copper(II) complexes. In other words, the concentration that can be determined polarographically is $[Cu^{2+}]_{app}$ given by the equation[4]

$$[Cu^{2+}]_{app} = [Cu^{2+}] + [CuOAc^+] + [Cu(OAc)_2] \quad (5)$$

The rate equation for reaction 4, therefore, is expressed as

$$-\frac{d[Cu^{2+}]_{app}}{dt} = k^+[Cu^{2+}]_{app} - k^-[CuY^{2-}] \quad (6)$$

Integrating Eq. 6,

$$\ln\{[Cu^{2+}]_{app} - [Cu^{2+}]_{e,app}\} = -(k^+ + k^-)t + \ln\{[Cu^{2+}]_{0,app} - [Cu^{2+}]_{e,app}\}$$

is obtained. At the equilibrium of the reaction, the relation

$$\frac{k^+}{k^-} = \frac{[CuY^{2-}]_e}{[Cu^{2+}]_{e,app}} \doteqdot K^{Cu}_{Pb,app}\frac{[PbY^{2-}]_0}{[Pb^{2+}]_{0,app}}$$

may be satisfied, where $K^{Cu}_{Pb,app}$ represents the apparent equilibrium constant expressed as

$$K^{Cu}_{Pb,app} = \frac{[Pb^{2+}]_{e,app}[CuY^{2-}]_e}{[Cu^{2+}]_{e,app}[PbY^{2-}]_e}$$

Subscripts e and 0 mean equilibrium and zero time, respectively. The value of $K^{Cu}_{Pb,app}$ must be determined polarographically as the same concentration of acetate as the reaction rate is observed.

In the previous study[1], it was found that the substitution reaction between copper(II) and lead-EDTA complexes proceeds through the simultaneous reaction paths

$$\text{(i)}\quad Cu^{2+} + PbY^{2-} \underset{k_I^-}{\overset{k_I^+}{\rightleftharpoons}} CuY^{2-} + Pb^{2+} \quad (7)$$

$$\text{(ii)}\quad PbY^{2-} + H^+ \rightleftharpoons PbHY^- \quad (8a)$$

$$Cu^{2+} + PbHY^- \underset{k_{II}^-}{\overset{k_{II}^+}{\rightleftharpoons}} CuHY^- + Pb^{2+} \quad (8b)$$

$$CuHY^- \rightleftharpoons CuY^{2-} + H^+ \quad (8c)$$

$$\text{(iii)}\quad PbY^{2-} + H^+ \rightleftharpoons Pb^{2+} + HY^{3-} \quad (9a)$$

$$Cu^{2+} + HY^{3-} \underset{k_{III}^-}{\overset{k_{III}^+}{\rightleftharpoons}} CuY^{2-} + H^+ \quad (9b)$$

and the rate equation

2) H. Ackermann and G. Schwarzenbach. *Helv. Chim. Acta*, **35**, 485 (1952).

3) N. Tanaka and K. Kato, unpublished work.

4) Cf., N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

$$-\frac{d[Cu^{2+}]}{dt}=\left\{k_1^{+}+k_2^{+}[H^+]+k_3^{+}\frac{[H^+]}{[Pb^{2+}]}\right\}\times[Cu^{2+}][PbY^{2-}]-\left\{k_1^{-}+k_2^{-}[H^+]+k_3^{-}\frac{[H^+]}{[Pb^{2+}]}\right\}[Pb^{2+}][CuY^{2-}] \quad (10)$$

was derived, where

$$\left.\begin{aligned} k_2^{+}&=k_{II}^{+}K_{PbHY}^{II}, & k_2^{-}&=k_{II}^{-}K_{CuHY}^{II}\\ k_3^{+}&=k_{III}^{+}/(K_{PbY}K_{HY}), & k_3^{-}&=k_{III}^{-}\end{aligned}\right\} \quad (11)$$

As has been mentioned above, the concentration which was actually measured polarographically was not the concentration of hydrated copper(II) ions in Eq. 10, but the sum of the concentrations of hydrated ions and acetato complexes. If it is assumed that the substitution reaction proceeds through only the hydrated ions which are in equilibrium with the acetato complexes, the apparent rate of the reaction ($=-d[Cu^{2+}]_{app}/dt$) which is determined polarographically is expressed as

$$-\frac{d[Cu^{2+}]_{app}}{dt}=\left\{k_1^{+}+k_2^{+}[H^+]+k_3^{+}\frac{[H^+]}{[Pb^{2+}]}\right\}\times[Cu^{2+}][PbY^{2-}]-\left\{k_1^{-}+k_2^{-}[H^+]+k_3^{-}\frac{[H^+]}{[Pb^{2+}]}\right\}[Pb^{2+}][CuY^{2-}] \quad (12)$$

From Eq. 5, the concentration of the hydrated copper(II) ions is given as

$$[Cu^{2+}]=\frac{[Cu^{2+}]_{app}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n} \quad (13)$$

where $K_{Cu(OAc)_n}$ represents the overall formation constant of acetatocopper(II) complexes expressed with

$$K_{Cu(OAc)_n}=\frac{[Cu(OAc)_n^{(2-n)+}]}{[Cu^{2+}][OAc^-]^n}$$

Similarly the concentration of the hydrated lead(II) ions is given as

$$[Pb^{2+}]=\frac{[Pb^{2+}]_{app}}{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}$$

where $K_{Pb(OAc)_n}$ means the overall formation constant of acetatolead(II) complexes.

Introducing Eqs. 13 and 14 into Eq. 12, Eq. 15 is obtained. Eq. 15 is now considered to be a general formula which expresses the rate of the substitution reaction between copper(II) and lead-EDTA complexes in acetate media.

Determination of the Rate Constants

From Eqs. 6 and 15, the relations given by Eqs. 16 and 17 are obtained, where the initial concentrations, $[Pb^{2+}]_0$ and $[PbY^{2-}]_0$, are substituted for $[Pb^{2+}]$ and $[PbY^{2-}]$, respectively. Since both $[Pb^{2+}]$ and $[PbY^{2-}]$ are present in the reaction mixture in a large excess over the concentration of copper(II), the changes of their concentrations during the reaction can be neglected.

$$-\frac{d[Cu^{2+}]_{app}}{dt}=\left\{\frac{k_1^{+}+k_2^{+}[H^+]+k_3^{+}[H^+]\dfrac{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}{[Pb^{2+}]_{app}}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n}\right\}[Cu^{2+}]_{app}[PbY^{2-}]-\left\{\frac{k_1^{-}+k_2^{-}[H^+]+k_3^{-}[H^+]\dfrac{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}{[Pb^{2+}]_{app}}}{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}\right\}[Pb^{2+}]_{app}[CuY^{2-}] \quad (15)$$

$$\frac{k^{+}}{[PbY^{2-}]_0}\equiv\frac{k_1^{+}+k_2^{+}[H^+]+k_3^{+}[H^+]\dfrac{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}{[Pb^{2+}]_{0,app}}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n} \quad (16)$$

$$\frac{k^{-}}{[Pb^{2+}]_{0,app}}\equiv\frac{k_1^{-}+k_2^{-}[H^+]+k_3^{-}[H^+]\dfrac{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n}{[Pb^{2+}]_{0,app}}}{1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n} \quad (17)$$

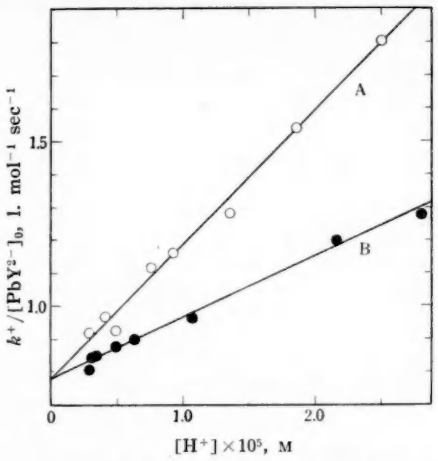

Fig. 1. $k^+/[PbY^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer—potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[Cu^{2+}]_{0,app}=1.86\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; $[Pb^{2+}]_{0,app}=3.95\times10^{-3}$ M (curve A) and 9.97×10^{-3} M (curve B). Concentratrations of free acetate are: 0.095 M (A) and 0.088 M (B).

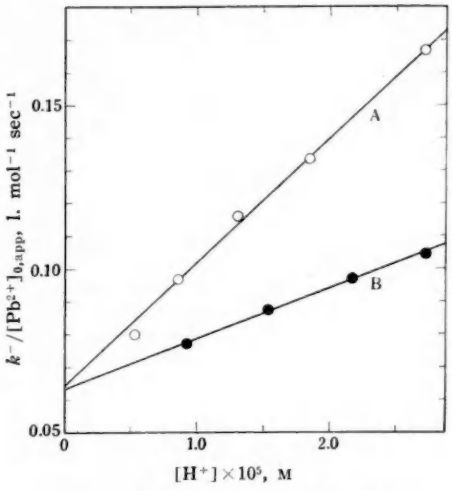

Fig. 2. $k^-/[Pb^{2+}]_{0,app}$ as a function of the hydrogen ion concentration in acetate buffer—potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[CuY^{2-}]_0=4.65\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; $[Pb^{2+}]_{0,app}=3.95\times10^{-3}$ M (curve A) and 9.97×10^{-3} M (curve B). Concentrations of free acetate are: 0.095 M (A) and 0.088 M (B).

The experimental results which were reported in the previous paper[1] were utilized for the calculation of the rate constants in Eq. 15. The relations of $k^+/[PbY^{2-}]_0$ vs. $[H^+]$ and $k^-/[Pb^{2+}]_{0,app}$ vs. $[H^+]$ are plotted in Figs. 1 and 2. The values of the rate constants calculated are given in Table I. The formation constants of acetatocopper(II) and acetatolead(II) complexes which were used in the calculation are those which were determined polarographically at ionic strength 0.2 at 15, 25 and 35°C[3]. They are given in Table II. The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

The rate constants of both elementary reactions 8b and 9b can be calculated from the relations given in Eqs. 11, using the values of K^H_{PbHY}, K_{PbY} and K_{HY} which are given in Table III. The values of K_{PbY} at 15, 25 and 35°C were obtained by dividing the values of K_{CuY} by those of K^{Cu}_{Pb}. The

Table I. Rate constants in Eq. 15 obtained experimentally at ionic strength 0.2 at various temperatures

Temp., °C	Rate constant, l. mol^{-1} sec^{-1}					
	k_1^+	k_2^+	k_3^+	k_1^-	k_2^-	k_3^-
15	1.7	6×10^3	18			
25	5.1	3×10^4	58	1.0	3×10^3	14
35	17	1.5×10^5	160			

Table II. Formation constants of acetato complexes of copper(II) and lead(II) at ionic strength 0.2 at various temperatures

Temp., °C	K_{CuOAc}	$K_{Cu(OAc)_2}$	K_{PbOAc}	$K_{Pb(OAc)_2}$
15	41	190	130	750
25	52	93	130	390
35	69	82	120	380

Table III. Equilibrium constants at ionic strength 0.2 at various temperatures

Temp., °C	log K_{PbY}	pK_{HY}	log K^H_{PbHY}
15	18.17	10.20	—
20	—	—	2.7
25	17.76	10.04	—
35	17.36	9.91	—

Table IV. Rate constants for reactions 7, 8b and 9b at ionic strength 0.2 at various temperatures

Temp., °C	Rate constant, l. mol^{-1} sec^{-1}		
	k_1^+	k_{II}^+	k_{III}^+
15	1.7	10	1.7×10^9
25	5.1	60	3.0×10^9
35	17	300	4.5×10^9

TABLE V. RATE CONSTANTS, HEAT OF ACTIVATION AND ENTROPY OF ACTIVATION FOR REACTIONS 7, 8b AND 9b

Reaction	Rate constant, expressed in l. mol^{-1} sec^{-1}	ΔH^*, kcal. mol^{-1}	ΔS^*, e. u.
$Cu^{2+}+PbY^{2-} \rightarrow CuY^{2-}+Pb^{2+}$	$k_1^+=2.7\times10^{15}\ \exp(-20{,}000/\boldsymbol{RT})$	19	10
$Cu^{2+}+PbHY^{-} \rightarrow CuHY^{-}+Pb^{2+}$	$k_{II}^+=2.5\times10^{22}\ \exp(-28{,}000/\boldsymbol{RT})$	27	42
$Cu^{2+}+HY^{3-} \rightarrow CuY^{2-}+H^+$	$k_{III}^+=3.2\times10^{15}\ \exp(-\ 8{,}200/\boldsymbol{RT})$	7.6	10

formation constants of CuY^{2-}, K_{CuY}, at 15, 25 and 35°C at ionic strength 0.2 were calculated, from the value obtained by Schwarzenbach et al.[5] at 20°C at ionic strength 0.1, with the aid of the Debye-Hückel equation and the heat of formation of CuY^{2-}, −8.2 kcal./mol., reported by Charles[6]. The equilibrium constants of reaction 2 at zero acetate concentration, K_{Pb}^{Cu}, used in this calculation are those determined by the present authors[3]. The rate constants of three elementary reactions 7, 8b and 9b thus calculated are summarized in Table IV.

Discussion

Linear relations were found between the logarithm of rate constant and the reciprocal of absolute temperature for three elementary reactions 7, 8b and 9b.

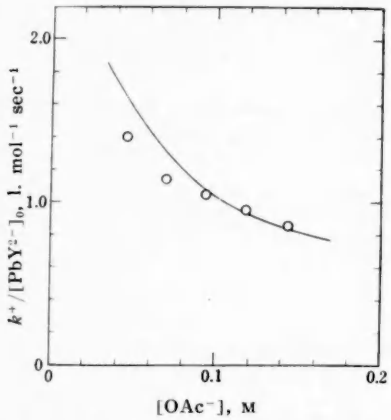

Fig. 3. $k^+/[PbY^{2-}]_0$ as a function of the acetate concentration in acetate buffer—potassium nitrate solutions of pH 5.14 and ionic strength 0.2 at 25°C. Initial concentrations are: $[Cu^{2+}]_{0,app}=1.96\times10^{-4}$ M; $[PbY^{2-}]_0=4.90\times10^{-3}$ M; $[Pb^{2+}]_{0,app}=4.90\times10^{-3}$ M. — indicates the theoretical curve and ○, the experimental value.

5) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).
6) R. G. Charles, *J. Am. Chem. Soc.*, **76**, 5854 (1954).

This made it possible to express the rate constants in the form of the Arrhenius equation and to calculate the heat of activation and the entropy of activation. The results are given in Table V.

From Eq. 15, it is predicted that the reaction rate decreases with the increase of acetate concentration. Using Eq. 16, the values of $k^+/[PbY^{2-}]_0$ were calculated at various acetate concentrations with the rate constants given in Table I and the formation constants of the acetato complexes. They are plotted against acetate concentration as shown in Fig. 3. The reaction rates were experimentally measured at various acetate concentrations, keeping the other conditions constant, with the same procedure as given in the previous paper[1]. Those values are also shown in Fig. 3, which are in fair agreement with the calculated ones. The deviation of the expermental values from the calculated ones is apparent at lower acetate concentration. This has not been clearly understood, but is considered to be due to a contribution of the reactions in which acetatocopper(II) complexes participate.

Summary

The effect of acetate ions on the rate of the substitution reaction of copper(II) and lead-EDTA complexes is explained quantitatively on the basis of the formation of acetato complexes of copper(II) and lead(II) in acetate media and on the assumption that the substitution reaction proceeds only through the hydrated metal ions. The rate constants, the heats of activation and the entropies of activation for three elementary reactions are recalculated with the experimental results obtained previously.

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SHORT COMMUNICATIONS

Infrared Spectra of Glycols Coordinated to Metal Ions

By Akihisa MIYAKE

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Ethylene glycol has received attention in discussion of the infrared spectrum of polyethylene glycol[1]. Certain problems with regard to the rotational isomerism of this molecule still remain to be solved. It has been known that ethylene glycol forms coordination compound with cobalt or nickel ion[2]. In an attempt to provide some new information on the vibrational assignments for this molecule, the infrared spectra of these coordination complexes were investigated.

Cobalt(II) chloride or nickel(II) chloride was dehydrated by heating at about 150°C. The coordination complexes were prepared by adding ethylene glycol to these dehydrated salts. There is a marked spectral difference between the free molecule and the molecule coordinated about a metal ion (Fig. 1). The coordinated ligand shows two kinds of spectra according to the water content of the dehydrated salts, both for cobalt and nickel. When the water contents of the salts exceed a value of about 15%, the complexes obtained from them (complex I) exhibit the spectrum shown in Fig. 1B. When the water contents are lower than this value, the complexes obtained (complex II) exhibit the spectrum shown in Fig. 1C. On the other hand, there is no difference between the cobalt and nickel complexes.

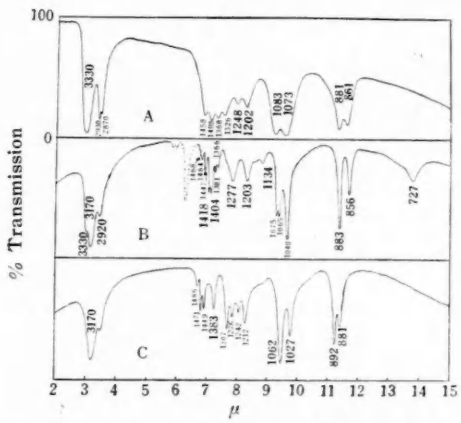

Fig. 1. Infrared spectra of ethylene glycol: (A) Liquid, (B) (C) metal complex (Nujol and polytrifluoroethylene mull, ---- water).

Two bands at 881 and 861 cm^{-1} in liquid ethylene glycol are undoubtedly assigned to the CH_2 rocking vibrations, because no other fundamental vibrations are expected in this region. The appearance of two CH_2 rocking bands indicates that ethylene glycol is present in the *gauche* form, because two CH_2 rocking bands (A and B types) are expected for the *gauche* form but only one (A_u type) for the *trans* form. The other CH_2 rocking vibration (B_g type) of the *trans* form is forbidden to appear in an infrared spectrum. An alternative interpretation is possible, however, assuming that two vibrations coalesce into a single band. In this way Kuroda and Kubo[1] have assigned the band at 881 cm^{-1} to the *gauche* form and the band at 861 cm^{-1} to the *trans* form, considering that the two *gauche* vibrations overlap. Experimental results obtained in the present work provide data as to which one of these contradictory interpretations is more reasonable.

The number of absorption bands observed in the spectra of the complexes is a little larger than that observed for the liquid state. This indicates that the number of molecular forms present in the complex is at least not smaller than that present in the liquid. Thus, if the *trans* and *gauche* forms coexist in the liquid, they must also coexist in the complexes. Then the bands at 887 cm^{-1} (complex I) and 892 cm^{-1} (complex II) must be assigned to the *gauche* form, and the bands at

1) Y. Kuroda and M. Kubo, *J. Polymer Sci.*, **26**, 323 (1957).
2) A. Grün and E. Boedecker, *Ber.*, **43**, 1051 (1910).

856 cm^{-1} (complex I) and 881 cm^{-1} (complex II) to the *trans* form. Relative intensities of these two bands attributed to different molecular forms do not change appreciably through the three states, liquid, complex I and complex II. Therefore, the assignment based on the coexistence of both *trans* and *gauche* forms leads to a very improbable conclusion that the equilibrium ratio of the two kinds of molecular form and hence the energy difference between them do not change through the three different states.

All the bands change their positions more or less on going from liquid to complex I and from complex I to complex II, indicating that some small differences in the molecular form are present among the three states. If the band at 881 cm^{-1} in liquid ethylene glycol is composed of two *gauche* vibrations, it is reasonably expected that these two separate from each other in the complexes because the CH_2 rocking frequencies are particularly sensitive to conformation[3]. Although the bands of the complexes at 887 and 892 cm^{-1} are much sharper than the band of the liquid at 881 cm^{-1}, there is no indication of such a separation. It is too accidental that the two *gauche* frequencies coincide through the three states.

From these considerations it is more reasonable to assign both the CH_2 rocking bands to the *gauche* form than to assign one of them to the *gauche* and the other to the *trans* form. The presence of only the *gauche* form is sufficient to account for the number of observed bands in the region 1500~800 cm^{-1}, ten for the liquid, fifteen for complex I, and thirteen for complex II. The number of fundamental frequencies expected to appear in this range are thirteen for the *gauche* form and six for the *trans* form.

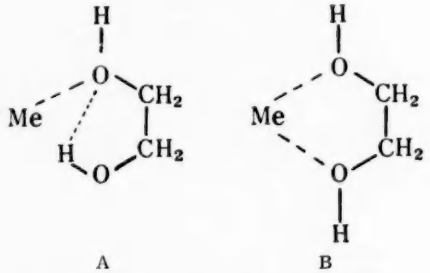

Fig. 2. Two types of coordination.

3) I. Nakagawa and S. Mizushima, This Bulletin, **28**, 589 (1955).

The ligand in complex I can be considered to coordinate in a manner shown in Fig. 2A. This is based on the existence of two OH bands (3330 and 3170 cm^{-1}) indicating the presence of two kinds of OH groups. [The OH frequencies of the coexisting water are higher (ca. 3400 cm^{-1}) even if they appear.] The ligand in complex II shows a single OH band and probably coordinates in a manner shown in Fig. 2B. Spectral features of the liquid ethylene glycol, especially the positions of the CH_2 rocking frequencies, are more close to those of complex I than to those of complex II. Thus one of the OH groups of ethylene glycol molecule seems to form an intramolecular hydrogen bond in the liquid state.

Besides ethylene glycol, diethylene glycol and triethylene glycol were also investigated. Again, there are significant changes of the spectra on passing from

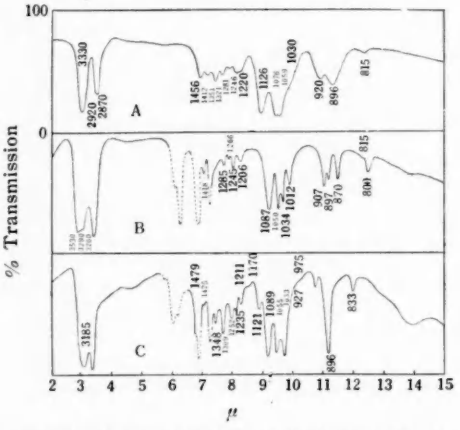

Fig. 3. Infrared spectra of diethylene glycol: (A) Liquid, (B) cobalt complex, (C) nickel complex (Nujol mull, ---- water and Nujol).

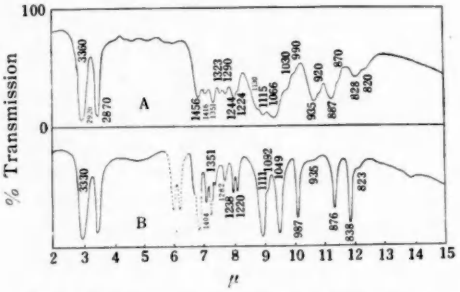

Fig. 4. Infrared spectra of triethylene glycol: (A) Liquid, (B) metal complex (Nujol mull, ---- water and Nujol).

liquid to complex compound. In the case of triethylene glycol, there is no difference between the spectra of nickel and cobalt complexes. On the other hand, in the case of diethylene glycol, the spectrum of the nickel complex differs profoundly from that of the cobalt complex (Fig. 3).

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Permeability of Amino Acid across Ion Exchange Membranes

By Takeo YAMABE, Manabu SENŌ and Nobuharu TAKAI

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The bulk of experimental work[1] has published on the separation of amino acids by ion exchange resins and a few studies[2], which dealt with electro-chemical desalting of amino acid solution using ion exchange membranes, have recently been presented. These electrodialyses of amino acids using ion exchange membranes were carried out in the range of pH higher than the isoelectric point of the amino acids and deep concerns were not paid for hydrogen ion concentration of sample solution by these authors. Since the charge carried by an ion of amino acid in its aqueous solution is greatly affected by pH of the medium, it is natural to expect that pH of sample solution is one of the greatest factors in the electrodialysis operation of amino acid.

In the present study, permeability of amino acid across ion exchange membranes was examined in the whole range of pH and some interesting results were found.

The apparatus consisted mainly of five-compartment cell which is shown shematically in Fig. 1. Into the center compartment, 0.05 N aqueous solution of glutamic acid containing sodium chloride

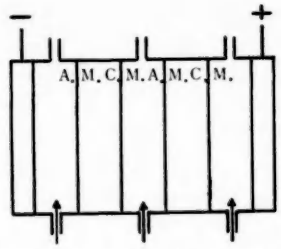

Fig. 1. Five compartment cell for electrodialysis.
C. M., cation exchange membrane
A. M., anion exchange membrane

(0.1 N), whose pH was adjusted with hydrochloric acid or sodium hydroxide beforehand, was fed at the flow-rate of 500 ml./hr. The two adjacent compartments, which are filled with 0.1 N sodium chloride, are separated from the center compartment by cation and anion exchange membranes, respectively. Amino acid transferred across each of these ion exchange membranes was measured.

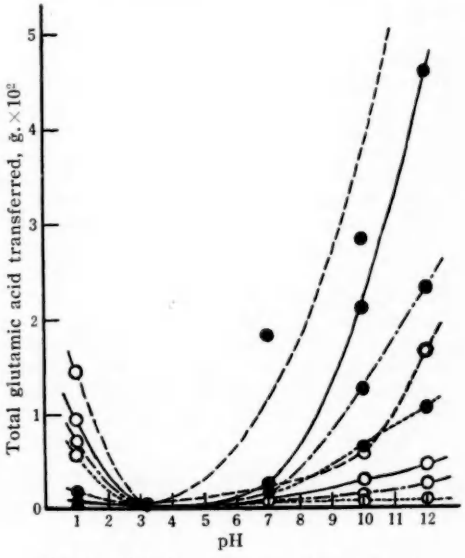

Fig. 2. Relation between pH and permeation of glutamic acid across ion exchange membranes.
○ permeation across cation exchange membrane
● permeation across anion exchange membrane
---------- 0.2×10^{-2} amp./cm²
—·—·— 0.5 〃
———— 1.0 〃
———— 2.0 〃

1) C. Calmon and T. R. E. Kressman, "Ion Exchangers in Organic and Biochemistry", Interscience Publishers, Inc., New York (1957).
2) J. D. Blainey and H. J. Yardley, *Nature*, **177**, 83 (1956); A. T. Di Benedetto and E. N. Lightfoot, *Ind. Eng. Chem.*, **50**, 691 (1958); A. M. Peers, *J. Appl. Chem.*, **8**, 59 (1958).

All the electrodialysis experiments were carried out for one hour at four fixed current densities. Ion exchange membranes used are heterogeneous and strongly dissociated ones are prepared in the authors' laboratory.

The results were given in Fig. 2. As seen in this figure, the permeability of amino acid depends greatly on the pH of medium and it is the lowest at the isoelectric point, pI 3.2, of glutamic acid. In the range of pH higher than pI, the larger parts of glutamic acid migrate through the anion exchange membrane to the anode-side and the permeation across the cation exchange membrane is predominant in the lower pH range. This behavior becomes more remarkable with the rise of current density. This result is reasonable in view of amphoteric nature of amino acid.

It must be pointed out that some parts of amino acid migrate in the direction unexpected and some amounts of amino acid permeate across the anion and the cation exchange membranes at the isoelectric point. It appears that both positively and negatively charged molecules of amino acid may exist in the moderate pH range, since it is clear that such a permeation of amino acid does not always take place only by the simple diffusion process through membranes as revealed by the experimental data when no electric current runs*. Further investigation must be done on this behavior.

The similar results were also obtained concerning the electro-chemical permeation of glycine and lysine. The full data will be presented in the near future.

From these results, the optimum pH in the separation of amino acids and the demineralization of amino acid solution by ion exchange membranes may be predicted. These experiments are now under study.

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* When no electric current is passed, the total amounts of glutamic acid transferred across ion exchange membranes are as follows:

pH	Total amounts of glutamic acid transferred across A. M.	C. M.
1.0	0	15.1×10^{-4} g.
3.2	0	0
12.0	95×10^{-4} g.	0

Absorption Spectra of 1,4-Diaminoanthraquinone in Mixed Solvents of Carbon Tetrachloride and Ethyl Alcohol

By Yoshio Suda

(Received October 21, 1959)

It was previously discussed by Arban[1,2] that the absorption spectra of methylene blue in mixed solvents of water and organic solvents showed characteristic shifts which might be attributed to the change in aggregation states of the dye ion in the mixed solvents.

In this paper, characteristic changes in spectra of 1,4-diaminoanthraquinone (DAA) in mixed solvents are reported. The spectra were measured by means of a Hitachi recording spectrophotometer model EPR and all the measurements were carried out with the 1.0×10^{-4} mol./l. solution of DAA. As shown in Fig. 1, the spectrum of DAA in carbon tetrachloride has one absorption peak I at

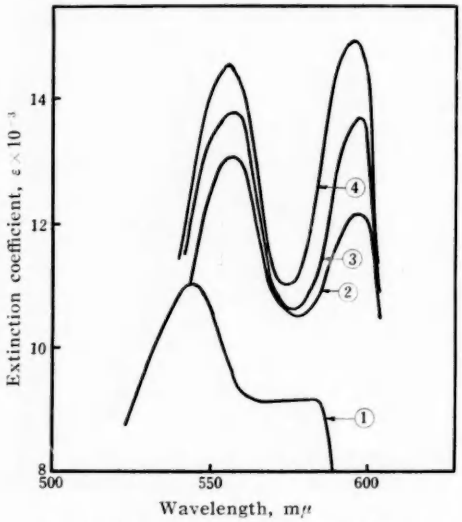

Fig. 1. Absorption spectra of 1,4-diaminoanthraquinone in mixed solvents; in CCl_4 ①, in CCl_4 80%: C_2H_5OH 20% ②, in CCl_4 40%: C_2H_5OH 60% ③, and in C_2H_5OH ④.

1) Kh. L. Arban, *Izves. Acad. Nauk USSR, Series Phys.*, **22**, 443 (1956).
2) Kh. L. Arban and N. V. Ivanova, *Doklady Acad. Nauk USSR*, **114**, 1043 (1957).

544 mμ and one horizontal shoulder at 565~584 mμ. On addition of ethanol to the solution, the latter changes to the second peak II, and simultaneously a shift of the peak location occurs. With the increasing ethanol concentration, the extinction coefficient at peak II increases rapidly as compared with that at peak I, and consequently, the ratio of both coefficients $r=\varepsilon_{II}/\varepsilon_{I}$ increases. The spectral data of DAA in various organic solvents are given in Table I. Solvents which belong to the first group are non-polar and the spectra in these solvents show one maximum and one shoulder, and a small value of r. In contrast to this, the spectra in solvents of the second group which are polar and have hydrogen-bonding ability, show the two absorption peaks and a large value of r.

TABLE I. ABSORPTION SPECTRA DAA IN VARIOUS SOLVENTS

Solvents	Refractive Index	Absorption peak I mμ	r
The first group			
n-Hexane	1.38	534	0.83
Cyclohexane	1.43	539	0.82
Carbon tetrachloride	1.46	544	0.83
Benzene	1.50	545	0.85
The second group			
Methanol	1.33	551	0.98
Ethanol	1.36	554	1.03
Acetic acid	1.37	552	1.03
Glycerine	1.47	557	1.05
Pyridine	1.51	558	0.94

An addition of ethanol to pure solvent exerts another effect on the spectrum. When the concentration of ethanol is increased, the location of the peak shifts to longer wavelengths at first and via the point of the maximum shift return back to shorter wavelengths. Similar shifts are also observed with methanol and others. As examples, absorption curves in mixed solvents of carbon tetrachloride with methanol and ethanol are shown in Fig. 2.

This characteristic change can not be explained by the simple solvent-effect (Kundt's law) alone, because the law says only that the larger the refractive index of solvent is, the larger the degree of shift to longer wavelengths becomes. DAA satisfies Beer's law both in ethanol and in carbon tetrachloride, and disperses as the monomer or a uniformly aggregated particle. Arban's suggestion for methylene blue does not explain the case of DAA, if it can be assumed that dispersed particles are monomers in both solutions.

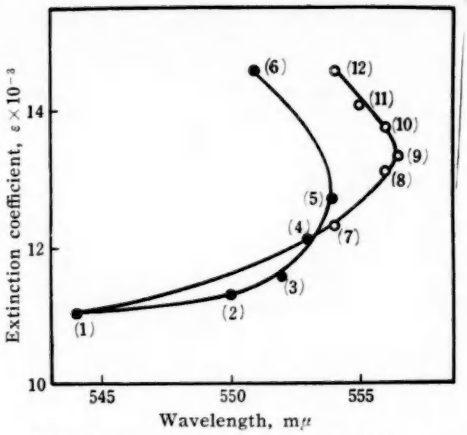

Fig. 2. Effects of solvent composition on wavelength and extinction coefficient at peak I.
—●— CH_3OH-HCl_4 mixtures
(1) 0 : 100, (2) 4 : 96, (3) 8 : 92
(4) 20 : 80, (5) 40 : 60 (6) 100 : 0
—○— C_2H_5OH-CCl_4 mixtures
(1) 0 : 100, (7) 6 : 94, (8) 20 : 80
(9) 40 : 60, (10) 60 : 40, (11) 80 : 20
(12) 100 : 0

Spectral differences such as a number of peaks, the ratio of extinction coefficients and characteristic changes of locations of peaks indicate that mutual interaction between DAA and carbon tetrachloride (the first group) differs from that between DAA and ethanol (the second group). The essential difference in the interaction has been studied by the present author from the view points of solubility. The detailed discussion on the results will be reproted elsewhere.

The author wishes to express his sincere thanks to Mr. H. Uedaira for helpful discussion and for a gift of copies of Arban's papers.

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Detection of Atomic Oxygen in the Decomposition Products of Nitrous Oxide by the Platinum Catalyst at Low Pressures

By Kazuo MITANI and Yoshio HARANŌ

(Received November 4, 1959)

Nitrous oxide is decomposed by platinum catalyst into oxygen and nitrogen. It is generally accepted that the first step of this reaction is $N_2O \rightarrow N_2 + O$; and that the nitrogen is given off from the surface, while the oxygen atom remains adsorbed. The authors have investigated to find whether this oxygen atom is given off in the atomic state into the gas phase at low pressures.

The main part of the apparatus is shown in Fig. 1.

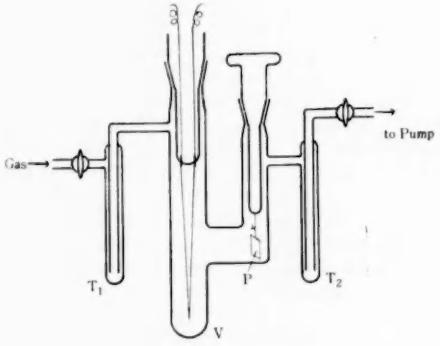

Fig. 1.

In the reaction vessel V, a platinum ribbon ($0.024 \times 0.28 \times 363$ mm.) is stretched, which can be heated by electric current. Atomic oxygen is detected by the change of color of molybdenum trioxide from pale yellow to deep blue according to the following equation[1]:

$$3\,MoO_3 + O = Mo_3O_8 + O_2$$

Molybdenum trioxide is deposited on a glass plate P, which is hung in the side tube of the reaction vessel. All the apparatus can be evacuated by a diffusion pump through a trap cooled by dry ice.

After decomposing nitrous oxide, it was found that atomic oxygen is given off from the platinum surface heated in vacuo for a long time[2]. Therefore, the following preliminary treatment of the platinum ribbon is necessary before every experiment. The platinum ribbon is heated in hydrogen first, and then in vacuo, to a high temperature. Subsequently oxygen is admitted, and the ribbon is heated again. Finally the ribbon is heated once more in vacuo to 1400°C for an hour. After this treatment, the platinum ribbon does not give off atomic oxygen. Now, nitrous oxide is conducted from the reservoir to the pump through the reaction vessel, the pressure in the reaction vessel being kept at $1 \times 10^{-3} \sim 5 \times 10^{-4}$ mmHg. When the platinum ribbon is heated to 1400°C, molybdenum trioxide changes its color distinctly from plale yellow to deep blue within 30 min. From this experiment it is certain that atomic oxygen is given off when nitrous oxide is decomposed by the platinum catalyst at low pressures. When the pressure of nitrous oxide is higher (0.1~0.03 mmHg), no atomic oxygen is detected in a similar experiment. In the latter experiment, oxygen atoms given off from the platinum surface may recombine to form molecular oxygen before reaching the detector of atomic oxygen. But it is also probable that nitrous oxide molecules collide from the gas phase to the adsorbed oxygen atoms very frequently when the pressure of nitrous oxide is higher, and that consequently adsorbed oxygen atoms are given off as molecular oxygen according to the following reaction:

$$O_{ads} + N_2O \rightarrow N_2 + O_2$$

In order to decide which mechanism is true, further investigations are necessary.

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1) W. H. Rodebush and W. A. Nichols, *J. Am. Chem. Soc.*, **52**, 3864 (1930).

2) A detailed report will be published in the near future.

Electrometric Estimation of Bismuth

By V. D. Anand, B. N. Prasad and Aqil Ahmed Amani

(Received June 8, 1959)

Thiourea and its derivatives, which are good sulfur coordinators[1], have been used for the detection and determination of a number of ions. Bismuth ion forms a yellow compound on the addition of thiourea[2]. Recently an electrometric study of the bismuth complexes with thiourea and substituted thioureas employing the bimetallic electrode system has been communicated by the anthors' laboratories[3]. During the course of this work it was observed that the method can be easily adopted for the quantitative determination of bismuth. The present communication reports in detail the application of the bimetallic electrode system to the estimation of bismuth with thiourea, substituted thioureas and urea.

B.D.H. reagent grade bismuth trichloride was recrystallized twice from acetone and its solutions of varying concentrations in anhydrous methanol, ethanol and acetone were prepared. The strength of these solutions was determined by the oxychloride method[4]. Thiourea solutions were standardized by the Volhard procedure[5] as modified by Cuthil and Atkins[6].

The bimetallic electrode system was used, employing the Pt : W bimetallic couple, first proposed by Furman and Wilson[7]. The Bi : W electrode system was also used. An aliquot of the bismuth chloride solution was taken in a pyrex cell fitted with the platinum and tungsten (or the bismuth and tungsten) electrodes. The electrical circuit was similar to that used by Gay[8], and consisted of a 1.5 V. cell with its negative pole connected to the tungsten electrode, a 1 kΩ fixed resistance, a 200 Ω variable rheostat and a suitably shunted galvanometer, all connected in series. Galvanometer deflections were noted after successive additions, from the burette, of small amounts of standard thiourea solution and thorough stirring.

The addition of the titrant near the end point was dropwise. Maxima in the galvanometric deflection mark the equivalence points, corresponding to the formation of different complexes.

A representative curve from an actual determination of bismuth against thiourea in acetone medium, using the Pt : W bimetallic electrode system, is shown in Fig. 1. The curve shows two peaks corresponding to the two complexes of bismuth with thiourea reported in the earlier communication[3].

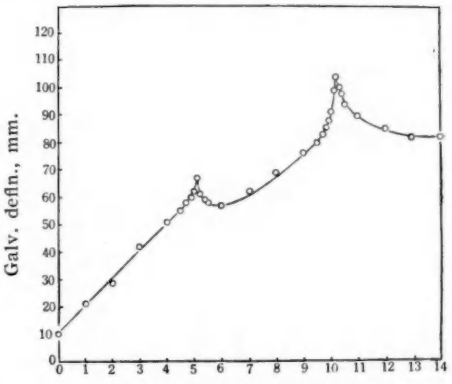

Fig. 1. Titration of bismuth against thiourea in acetone medium, using Pt: W bimetallic electrode system.

Table I shows the results of determination of bismuth against thiourea, phenyl thiourea, *p*-toluyl thiourea and urea in different non-aquous media using the Pt : W bimetallic system.

The estimation of bismuth against the same ligands was also done with the Bi : W bimetallic electrode couple. The results are recorded in Table II. The titrations with urea had to be restricted to methanol and ethanol medium only because of the low solubility of urea in acetone.

The two peaks in the titration curve correspond to the two end points in these titrations. This agrees with the formation of the two complexes viz., $2BiCl_3 \cdot 3X$ and

1) J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942).
2) C. Mahr, *Z. anal. Chem.*, **94**, 161 (1933); **97**, 96 (1934).
3) V. D. Anand and B. N. Prasad, communicated to *Z. anorg. u. allgem. Chem.* (accepted for publication).
4) "Scotts Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand Co., Inc., New York (1944), p. 153.
5) J. Volhard, *Ber.*, **7**, 100 (1847).
6) R. Cuthil and C. Atkins, *J. Soc. Chem. Ind.*, **56**, 5T (1937).
7) N. H. Furman and E. B. Wilson, *J. Am. Chem. Soc.*, **50**, 277 (1928).
8) J. R. Gay, *Ind. Eng. Chem., Anal. Ed.*, **11**, 383 (1939); cf. A. Findlay, "Practical Physical Chemistry", Longman Green and Co., Inc., London (1949), p. 240.

TABLE I. ELECTROMETRIC DETERMINATION OF BISMUTH
(Pt : W Bimetallic electrode system)

Solvent medium	Weight of the bismuth complex					
	$2BiCl_3 \cdot 3X$*			$BiCl_3 \cdot 3X$*		
	Calculated g.	Found g.	Error mg.	Calculated g.	Found g.	Error mg.
			Thiourea			
Acetone	0.1428	0.1430	+0.2	0.1809	0.1811	+0.2
	0.0142	0.0142	—	0.0180	0.0181	+0.1
	0.0072	0.0072	—	0.0091	0.0090	−0.1
Methanol	0.0812	0.0815	+0.3	0.1028	0.1026	−0.2
	0.0162	0.0164	+0.2	0.0205	0.0204	−0.1
	0.0041	0.0040	−0.1	0.0052	0.0052	—
Ethanol	0.1290	0.1293	+0.3	0.1631	0.1635	+0.4
	0.0257	0.0258	+0.1	0.0325	0.0327	+0.2
	0.0129	0.0129	—	0.0163	0.0162	−0.1
			Phenyl thiourea			
Acetone	0.0180	0.0184	+0.4	0.0255	0.0252	−0.3
	0.0091	0.0092	+0.1	0.0129	0.0128	−0.1
	0.0044	0.0046	+0.2	0.0063	0.0064	+0.1
Methanol	0.0689	0.0685	−0.4	0.0979	0.0972	−0.7
	0.0346	0.0344	−0.2	0.0491	0.0488	−0.3
	0.0138	0.0137	−0.1	0.0196	0.0194	−0.2
Ethanol	0.0359	0.0357	−0.2	0.0510	0.0514	+0.4
	0.0180	0.0180	—	0.0255	0.0256	+0.1
	0.0073	0.0073	—	0.0103	0.0102	−0.1
			p-Toluyl thiourea			
Acetone	0.0426	0.0423	−0.3	0.0614	0.0609	−0.5
	0.0212	0.0212	—	0.0305	0.0302	−0.3
	0.0084	0.0083	−0.1	0.0121	0.0121	—
Methanol	0.0513	0.0508	−0.5	0.0739	0.0745	+0.6
	0.0258	0.0255	−0.3	0.0371	0.0372	+0.1
	0.0103	0.0102	−0.1	0.0149	0.0149	—
Ethanol	0.0253	0.0250	−0.3	0.0365	0.0363	−0.2
	0.0128	0.0128	—	0.0184	0.0185	+0.1
	0.0052	0.0052	—	0.0074	0.0074	—
			Urea			
Methanol	0.0764	0.0768	+0.4	0.0934	0.0939	+0.5
	0.0382	0.0383	+0.1	0.0467	0.0465	−0.2
	0.0192	0.0192	—	0.0234	0.0233	−0.1
Ethanol	0.1125	0.1133	+0.8	0.1375	0.1364	+1.1
	0.0225	0.0227	+0.2	0.0275	0.0272	−0.3
	0.0112	0.0111	−0.1	0.0137	0.0137	—

* X denotes the complexing ligand.

$BiCl \cdot 3X$ (Where X stands for the complexing group). The two end points afford a convenint internal check on the accuracy of the procedure. The titration may, however, be stopped at either stage, since both equivalence points give accurate values within the limits of experimental error and results are easily reproducible.

It is evident from an examination of Tables I and II that the error is generally small and far less than is usually met with in the ordinary estimations. This is indicative of the fact that the electrometric determination is a simple, convenient and rapid procedure, easily applicable to the quantitative determination of bismuth.

TABLE II. ELECTROMETRIC DETERMINATION OF BISMUTH
(Bi : W Bimetallic electrode system)

Solvent medium	Weight of the bismuth complex					
	$2BiCl_3 \cdot 3X$*			$BiCl_3 \cdot 3X$*		
	Calculated g.	Found g.	Error mg.	Calculated g.	Found g.	Error mg.
			Thiourea			
Acetone	0.1428	0.1437	+0.9	0.1809	0.1823	+1.4
	0.0142	0.0143	+0.1	0.0180	0.0182	+0.2
	0.0072	0.0072	—	0.0091	0.0090	−0.1
Methanol	0.0812	0.0806	−0.6	0.1028	0.1020	−0.8
	0.0162	0.0163	+0.1	0.0205	0.0208	+0.3
	0.0041	0.0041	—	0.0052	0.0052	—
Ethanol	0.1290	0.1298	+0.8	0.1631	0.1640	+0.9
	0.0257	0.0259	+0.2	0.0325	0.0328	+0.3
	0.0129	0.0128	−0.1	0.0163	0.0164	+0.1
			Phenyl thiourea			
Acetone	0.0180	0.0182	+0.2	0.0255	0.0258	+0.3
	0.0091	0.0091	—	0.0129	0.0131	+0.2
	0.0044	0.0045	+0.1	0.0063	0.0063	—
Methanol	0.0689	0.0684	−0.5	0.0979	0.0983	+0.4
	0.0346	0.0344	−0.2	0.0491	0.0493	+0.2
	0.0138	0.0138	—	0.0196	0.0195	−0.1
Ethanol	0.0359	0.0362	+0.3	0.0510	0.0506	−0.4
	0.0180	0.0180	—	0.0255	0.0254	−0.1
	0.0073	0.0072	−0.1	0.0103	0.0103	—
			p-Toluyl thiourea			
Acetone	0.0426	0.0429	+0.3	0.0614	0.0618	+0.4
	0.0212	0.0214	+0.2	0.0305	0.0303	−0.2
	0.0084	0.0084	—	0.0121	0.0122	+0.1
Methanol	0.0513	0.0508	−0.5	0.0739	0.0733	−0.6
	0.0258	0.0256	−0.2	0.0371	0.0368	−0.3
	0.0103	0.0104	+0.1	0.0149	0.0149	—
Ethanol	0.0253	0.0255	+0.2	0.0365	0.0361	−0.4
	0.0128	0.0126	−0.2	0.0184	0.0182	−0.2
	0.0052	0.0052	—	0.0074	0.0073	−0.1
			Urea			
Methanol	0.0764	0.0769	+0.5	0.0934	0.0944	+1.0
	0.0382	0.0384	+0.2	0.0467	0.0470	+0.3
	0.0192	0.0193	+0.1	0.0234	0.0236	+0.2
Ethanol	0.1125	0.1136	+1.1	0.1375	0.1361	−1.4
	0.0226	0.0228	+0.2	0.0275	0.0272	−0.3
	0.0112	0.0113	+0.1	0.0137	0.0136	−0.1

* X denotes the complexing ligand.

Sincere thanks of the authors are due to Professor S. S. Joshi, D. Sc. (London), Head of Chemistry Department for facilities and keen interest and the Ministry of Scientific Research and Cultural Affairs for the award of a scholarship to one of them (V. D. A.).

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Additions and Corrections

Volume 30, 1957

K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya: Studies on Crystals of Metallic Tris-ethylenediamine-complexes. II.

Page 159. In col. 2, line 6 from the bottom, delete (000*l*), substitute (0001).
Page 160. In col. 2, line 5, delete $(P)VW$, substitute $P(VW)$.
Page 161. In col. 1, line 10 from the bottom, delete $I(hki1)$, substitute $I(hkil)$.
Page 162. In Table III, in footnote, delete period, substitute comma, add "with positive values of l.".
Page 163. In col. 2, line 40 delete $P\bar{3}cl$, substitute $P\bar{3}c1$.

S. Yamana: Molecular Rotations of Glucides in Relation to their Structures. II.

Page 207. In footnote 1), for "1953" read "1935"
Page 209. In Table I, for "$(3/n^2+2,)$" read "$(3/n^2+2)$,".
Page 210. In col. 2, line 21, for "adoption" read "adopting".

Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya: Studies on Crystals of Metallic Tris-ethylenediamine-complexes. III.

Page 795. In col. 2, line 19, delete $I_l(hkl) \geqslant I_l(\bar{h}\bar{k}\bar{l})$, substitute $I_l(hkl) \leqslant I_l(\bar{h}\bar{k}\bar{l})$.
Page 795. In col. 2, line 26, delete λ_k, substitute λ_K.
Page 796. In col. 2, line 3, delete $(hkil)$, substitute $(hkil\bar{)}$.
Page 796. In col. 2, line 13, delete $(32\bar{5}\bar{2})$, substitute (3252).
Page 796. In col. 2, line 14, delete $(32\bar{5}2)$, substitute $(32\bar{5}\bar{2})$.
Page 796. In col. 2, line 4 from the bottom, delete $F(hki\overline{2n})$, substitute $F(hki\overline{2n})$.
Page 797. In Table I, col. 1, add bars on 3rd figures, thus $10\bar{1}2$, $11\bar{2}\bar{2}$ etc.
Page 798. In col. 1, line 4, delete "inqeuality", substitute "inequality".

S. Yamana: Molecular Rotations of Glucides in Relation to their Structures. III.

Page 916. In col. 1, line 1 and in footnote *1, for "vant't" read "van't".
Page 916. In footnote 1), for "Van't" read "van't".
Page 917. In footnote *3, add ")" at the end.
Page 919. In col. 1, line 14, for "subtacting" read "subtracting".

S. Yamana: Molecular Rotations of Glucides in Relation to their Structures. IV.

Page 920. In col. 1, line 3 from the bottom, add "-" between "C^6" and "atom".
Pages 921 and 922. For all "P"s and "Q"s read "P"s and "Q"s.
Page 922. In col. 1, line 12 from the bottom, for "=" read "$\simeq$".
Page 922. In col. 1, line 1 of the footnote, for "8*" read "*8".
Page 922. In footnote *9, for "1β" read "(1β)" and for "$=0$" read "$\simeq 0$".

Additions and Corrections

Volume 31, 1958

S. Yamana: Molecular Rotations of Glucides in Relation to their Structures. V.

Page 558. At the top of the first sentence, for "On" read "Lately, on".
Page 558. In col. 1, line 5, for "this" read "that".
Page 558. In col. 2, line 1, for "bo nd a" read "bond at".
Page 559. In footnote *13, for "$(1/R^3_{ik})$" read "$(1/R^2_{ik})$".
Page 560. In footnote *19, for "angles" read "angle".
Page 561. In col. 1, line 11 from the bottom, for "ring" read "Ring".
Page 561. In Tables III and IV and col. 2, for all "R"s read "R"s.
Page 562. In col. 1, line 12, for "6" read "9".
Page 562. In col. 1, in footnote, line 15, for "$[\mu]^{20}_{Dobs}$" read "$[\mu]^{20}_{Dobs}$".

S. Yamana: Molecular Rotations of Glucides in Relation to their Structures. VI.

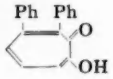
Page 564. In footnote a), for "Saccharimentry" read "Saccharimetry".

Page 566. In footnote *10, for "article" read "article.".
Page 568. In footnote *29, and "∴" between ";" and "{52.8".

H. Watase, Y. Tomiie and I. Nitta: The Structure of Kainic Acid, the Most Active Component of Digenea Simplex Ag. II.
Page 723. In col. 1, line 12, for
"$U(h0l)$, $K=|F'(h0l)|\exp B(\sin\theta/\lambda)^2/\sum f_i$" read
"$U(h0l)=K|F'(h0l)|\exp B(\sin\theta/\lambda)^2/\sum f_i$".

F. Ichikawa: A Study on Anion Exchange Separation of Neptunium from Irradiated Uranium.
Page 778. In col. 2, line 6, between "and" and "then", add "poured onto the resin column (1 cm.×6 cm.). The fission products are washed with 7.5 N nitric acid and".

T. Mukai: Reaction of Troponoids and Organometallic Compounds. III.
Page 854. Formula IV should read



Additions and Corrections

Volume 32, 1959

K. Hata, K. Watanabe and H. Watanabe: Catalytic Hydrogenation in Vapor Phase with Urushibara Nickel Catalyst.
Page 7. In footnote 5), for "Sci. Papers Inst. Phys. Chem. Research" read "Bull. Inst. Phys. Chem. Research".

M. Mori, S. Ueshiba and H. Yamatera: Photometric Study on the Change of Basic Rhodochromium Ion to Basic Erythrochromium Ion in Aqueous Solution.
Page 90. In col. 2, line 18, for "$\Delta S^*=2$ kcal/deg. mole" read "$\Delta S^*=2$ cal/deg. mole".

M. Muramatsu: Studies on the Interaction of Surface Films with Solute in Solution. IV.
Page 114. In col. 2, line 5, for "used also in of the present" read "used also in the present".
Page 114. In col. 2, line 6, for "alcohol was first" read "alcohol was of first".
Page 114. In Fig. 1, abscissa, for "Å A, ^{2}/molecule" read "A, Å^2/molecule".
Page 116. In col. 2, line 29, for "groups" read "group".
Page 117. In col. 1, line 4 from the bottom, for "AJ_0" read "ΔA_0".

Y. Sasada: Crystal and Molecular Structure of 1-Oxa-azulan-2-one. I.
Page 169. In Fig. 4, at the lower left-hand corner, for "1 0 2" read "1 0 1".

T. Arai: The Electrolytic Reduction of Ketones at a Mercury Cathode.—Preparation of Organomercuric Compounds.
Page 185. In col. 1, line 13, for "consisting" read "consisted".
Page 187. In col. 2, line 39, for "diisopropylmercury" read "bis-(1-benzylethyl)mercury".

A. Shimada: The Crystal Structure of Phenylarsonic Acid.
Page 309. In col. 2, line 12, for "D_{4l2}^4" read "D_2^4".
Page 309. In col. 2, line 37, for "$B=4.2$ Å^{-2}" read "$B=4.2$ Å^2".

C. Tamura, Y. Sasada and I. Nitta: Crystal Structure of 2-Chloro-1-aza-azulene.
Page 458. In col. 1, line 6 from the bottom, for "$^2_2C_h$" read "C_{2h}^5".

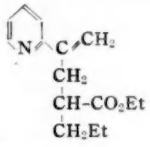
S. Yamana: Molecular Rotations of Glucides in Relation to their Structures. VII.
Page 597. In footnote 7), insert "ibid.," in front of "85,".
Page 598. In footnote 19), for "C*" read "O*".
Page 598. In footnote 20), for "orientationchange" read "orientation-change".
Page 598. In footnote 22), for "canceling" read "cancelling".

K. Fujimori: The Normal Vibrations of Methanesulfonate Ion.
Page 622. In col. 2, line 6 from the end, for "H_{Me-S}" read "K_{Me-S}".

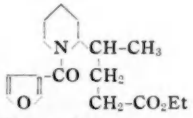
K. Fujimori: The Infrared Spectra of Alkane-1-sulfonates.
Page 852. In col. 1, lines 8 and 9 from the end, for "this CH_2 rocking vibration of $-(CH_2)_n-$ group" read "this CH_2 rocking vibration. The rocking vibration of $-(CH_2)_n-$ group".

M. Kotake, I. Kawasaki, T. Okamoto, S. Kusumoto and T. Kaneko: The Synthesis of *dl*-4-(3-Furyl)-1-methyl Quinolizidine; Demethyl Analogue of Deoxynupharidine.

Page 892. Formula II should be



Page 892. Formula V should be



Page 1153. On Miyaconitine and Miyaconitinone:

By Shichiro Kakimoto, Nobukatsu Katsui and Yoshiyuki Ichinohe (printed erroneously as Shichiro Kakimoto, Nobukatsu Katsui and Yoshiyuki Ichinose).

S. Hirota and M. Takada: Analysis of Non-Newtonian Flow By Falling-Sphere Method.

Page 1191. In col. 1, line 8, for "measunement" read "Measurement".

Page 1191. In col. 2, line 6. for "establishing" read "in establishing".

Page 1191. In footnote 10), for "(1956)" read "(1959)".

Page 1192. In col. 1, in Eq. 12, for "$(1/R^2)\cdot\int_R^\infty g(r)/r^4\cdot dr$" read "$(1/R^2)\cdot\int_R^\infty g(r)/r^2\cdot dr$".